Fuel 209 (2017) 184–193

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Modeling, simulation and kinetic parameter estimation for diesel hydrotreating

Leandro da Rocha Novaes, Neuman Solange de Resende, Vera Maria Martins Salim, Argimiro Resende Secchi*

Programa de Engenharia Química/COPPE – Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro 21941-972, RJ, Brazil

ARTICLE INFO

Keywords:
Hydrotreating
Modeling
Parameter estimation
Experimental planning
Internal diffusion

ABSTRACT

The modeling and simulation of hydrotreating (HDT) reactors can provide relevant information about optimal operating conditions, reactor design and formulation of catalysts to achieve cleaner fuels. This study developed a phenomenological model to estimate the kinetic parameters for the HDT process using the design of experiments technique. The catalytic tests were carried out in a bench-scale unit with diesel as feedstock under similar conditions to those of the industrial units and commercial nickel-molybdenum on alumina ($NiMo/\gamma\text{-}Al_2O_3$) as catalyst. The reactor temperature was varied from 330 to 380 °C and liquid hourly space velocity (LHSV) from 0.5 to 1.5 h^{-1}, keeping constant hydrogen to oil ratio (H_2/oil) and pressure at 800 std m^3/m^3 and 90 bar, respectively. The unknown parameters are estimated from experimental data by minimization of the unweighted least-squares function, using a non-linear optimization method (complex algorithm). The proposed model was able to reproduce different operating conditions with good adjustment and accuracy. Relative deviations below 4% for the experimental data and model prediction were achieved. Statistical parameters, p values, and confidence intervals confirmed the good quality of the estimated kinetic parameters. Internal diffusion resistances were present during hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions. The hydrogen consumption for HDS was higher than for HDN reaction. Finally, the proposed experimental design with 12 catalytic tests was satisfactory to obtain the desired results in a reliable way.

1. Introduction

Global crude oil production has increased around 12–13 million barrels from 2008 to 2017 [1]. Mostly applied in the transportation sector, it is expected that fossil fuels still account for more than three-quarters of world energy consumption through 2040. U.S. Energy Information Administration (EIA) projects that world energy consumption will keep growing by 48% between 2012 and 2040 [2]. In Brazil, the economic growth has substantially increased the production, processing and sale of diesel oil. From 2000 to 2015, the total demand of this type of fuel almost doubled, going from 220 to 377 million barrels [3]. On the other hand, there is a growing level of environmental awareness related to air quality and health impacts due to greenhouse gas effects. As consequence, stricter environmental legislation imposes severe restrictions on emissions of SO_x, NO_x, CO, CO_2, volatile organic compounds, and particulates from burning of fossil fuels. Therefore, the improving of fuels quality is essential for the oil sector in order to obtain both rentable and high quality distillates.

Catalytic hydroprocessing or hydrotreating (HDT) is fundamental in oil refineries to minimize the atmospheric emission through the removal or reduction of impurities (sulfur and nitrogen compounds), metals and undesirable compounds, such as aromatics in a wide variety of petroleum fractions [4]. Typically, the catalyst bed is composed of NiMo/CoMo alumina supported catalysts designed for HDT reactions: hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrogenation of aromatics (HDA) and hydrodemetallization (HDM). A preliminary study of the optimum operating conditions, e.g. pressure, temperature, space velocity and H_2/oil ratio, of industrial plants is required to achieve higher impurities removal. In addition, the choice of bed composition, type and configuration of the reactors are also of highest importance.

Mathematical models can be employed in optimizing and design purposes in engineering. They are usually cheaper and faster tools to evaluate the impacts of changes in variables, such as operating conditions on system performances. Besides, for the HDT process, the model development is a hard task in view of the chemical reactions, the

* Corresponding author.
E-mail addresses: lnovaes@peq.coppe.ufrj.br (L.d.R. Novaes), neuman@peq.coppe.ufrj.br (N.S. de Resende), vera@peq.coppe.ufrj.br (V.M.M. Salim), arge@peq.coppe.ufrj.br (A.R. Secchi).

http://dx.doi.org/10.1016/j.fuel.2017.07.092
Received 30 April 2017; Received in revised form 21 July 2017; Accepted 24 July 2017
Available online 29 July 2017
0016-2361/

Nomenclature

a^L	gas-liquid interfacial area, cm^{-1}
a^S	liquid-solid interfacial area, cm^{-1}
C_i	molar concentration of compound i, mol/cm^3
C_{H2}	molar concentration of H_2 at the inlet to the reactor, mol/cm^3
C_S	molar concentration of sulfur compounds at the inlet to the reactor, mol/cm^3
C_N	molar concentration of nitrogen compounds at the inlet to the reactor, mol/cm^3
$D_{ef,i}{}^L$	effective diffusivity of component i within the porous catalyst (cm^2/s)
d_{pe}	particle size, cm
D_r	reactor diameter, cm
Ea_j	activation energy for reaction j, kJ/mol
H_i	Henry's coefficient for compound i, MPa.cm^3/mol
g	acceleration of gravity, cm/s^2
$k_{0,j}$	pre-exponential factor of reaction j
k_j	reaction rate coefficient of reaction j
K_{H2S}	adsorption equilibrium constant of H_2S, cm^3/mol
$k_i{}^L$	gas-liquid mass transfer coefficient for compound i, cm/s
$k_i{}^S$	liquid-solid mass transfer coefficient for compound i, cm/s
L_B	catalyst bed length, cm
m_j, n_j	reaction orders (j = HDS, HDN)
p_i	partial pressure of compound i, MPa
p_{H2}	partial pressure of H_2 at the inlet to the reactor, MPa
S	value of optimized objective function
S_p	total external surface area of the catalyst particle (cm^2)
r_j	reaction rate, mol/cm^3/s
R	universal gas constant, J/(mol.K)
T	reaction temperature, K
u^L	superficial velocity of liquid, cm/s
u^G	superficial velocity of gas, cm/s
V_p	total volume of the catalyst particle (cm^3)
z	reactor bed length, cm

Greek letters

η_j	effectiveness factor for reaction j
ξ	ratio of the catalyst bed diluted by inert particles
ρ_b	bulk density of the catalyst, g/cm^3
ρ_S	catalyst density, g/cm^3
ρ^L	liquid-phase density, g/cm^3
μ^L	liquid-phase viscosity (cP)
Φ_j	Thiele module for reaction j
τ_s	form factor
Γ	concentration of sulfur and nitrogen in the product at the outlet of the bed

Superscripts

G	gas phase
L	liquid phase
S	solid phase

physicochemical changes in the feed (density, viscosity, solubility, vaporization) together with the transport phenomena that occur simultaneously in the fixed bed reactor. Korsten and Hoffman [5], in a great contribution in this field, proposed a model that included mass balances based on the two-film theory to consider transport effects between the phases and correlations to estimate the coefficients of mass transfer, gas solubility and oil properties. Also, the kinetic rate expression was based on Langmuir-Hinshelwood model to consider the inhibitor effect of hydrogen sulfide on HDS reactions. HDT models have several applications in engineering design and optimization, e.g. the simulation of an industrial unit with multi-bed adiabatic reactors and hydrogen quenching [6] or the evaluation of the effects of liquid and gas quench streams in heavy oils hydroprocessing [7]. Moreover, dynamic models that takes into consideration the main HDT reactions and different operation modes (cocurrent and countercurrent) have been applied to predict the behavior and performance of industrial hydrotreating reactors within a wide range of operating conditions [8–11].

Besides the model development, it is crucial that the proposed kinetic expressions allow the prediction of the product composition under different process conditions. This, however, is not a simple assignment because there are several chemical structures (mercaptans, thiophenes, pyridines, carbazoles, olefins, aromatics rings) that react simultaneously on the catalyst surface. In this scenario, the accurate and reliable estimation of kinetic parameters appears as a relevant purpose for HDT modeling studies [12–15]. There are several optimization techniques related to parameter estimation problems. Among them, nonlinear methods are the most popular and commonly applied to calculate optimal kinetic parameters, e.g. stochastic methods, particle swarm optimization and Levenberg-Marquardt methods [16–19]. Jarullah et al. [20] proposed a total of 27 experiments with three operating variables: pressure, temperature and liquid hourly space velocity (LHSV). They used a linear and non-linear approach to estimate HDS kinetic parameters. Although the results of the model simulations were according to experimental data, this number of tests can be hard to perform on hydrotreating pilot units due to long time duration and high costs.

Despite a large number of studies on HDT reactor modeling in literature, the experimental procedures described for kinetic parameter estimation might not be well designed and performed to optimize the reaction variables so as to obtain significant and precise results. Moreover, the reliability of the estimated kinetic parameters is not always clearly demonstrated by using statistical parameters (confidence intervals and p-value), sensitivity analysis or predictive capacity of the developed model. In view of this, the main focus of this study is the estimation of kinetic parameters for HDS and HDN reactions based on experimental data. The operational variables, temperature and LHSV were related to the parameters by using the design of experiments technique, aiming a good fit of the proposed model to the experimental data. A full factorial design 2^2 with three replicates in the central condition plus five additional experiments were proposed for the optimization step. A bench-scale unit with a medium distillate as feedstock was used under similar operating conditions to those of industrial hydrotreating units. The reactor model included mass-transfer resistances between the gas-liquid and liquid-solid interfaces and internal diffusion resistance. The kinetic parameters (reaction orders, reaction rate coefficients and activation energies) were obtained by minimizing the sum of the squared error between the experimental data and model prediction. Also, statistical, sensitivity and predictive analyses of the estimated parameters were performed. Evaluation of the catalyst effectiveness factor for both reactions was carried out under different operating conditions. Finally, the hydrogen consumption for both reactions, HDS and HDN, were obtained. The validated model was applied for HDT process simulation by using EMSO software.

2. Experimental

2.1. Catalyst

The catalytic tests were performed using a commercial HDT catalyst, nickel-molybdenum on alumina (NiMo/γ-Al_2O_3), having the