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Study and modeling of simultaneous hydrodesulfurization, hydrodenitrogenation and hydrodearomatization on vacuum gas oil hydrotreatment

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Abstract

One of the objectives of the present work is to expose the use of a trickle bed reactor model to predict the quality of products during the hydrotreatment of vacuum gas oil using a commercial catalyst and based on data obtained at pilot-plant scale, where catalytic experiments were carried out under typical industrial considerations, at different temperatures, pressures, and space-velocity (LSHV).

Most of the models only consider the hydrodesulfurization reaction (HDS). However, models that involve hydrogenation of aromatics (HDA) and hydrodenitrogenation (HDN) are scarce in the literature, and they are also very important for hydrotreatment reactor modeling, because mainly to news maximum limits in aromatics and nitrogen.

A sequential design of experiments was used for model discrimination and parameter estimation during kinetic investigation. Also, was investigated the effect of aromatics molecules (naphthalene, phenantrene) and nitrogen containing compounds (carbazol, acridine) on the HDS of a vacuum gas oil (VGO).

The reactor was simulated with a steady-state one-dimensional heterogeneous model. In addition, all necessary thermophysical properties, such as phase densities, viscosities, conductivities, diffusivities, and molar partial enthalpies were continuously calculated as functions of the system pressure, temperature and phase composition.

Keywords: Modeling, simulation, HDS, HDN, HDA

1. Introduction

Research on the purification of fuels, including desulfurization, denitrogenation, and dearomatization, has been come an important subject of environmental catalysis studies worldwide. Catalytic hydrotreating (HDT) is one of the most important processes in the petroleum refining industry, and it is applied to treat a great variety of refinery streams. The main differences for the HDT processes of each feed are operating conditions (temperature, H2 partial pressure, H2/Oil, LHSV), type of catalyst, reactor configuration, and reaction system (Rodriguez and Ancheyta, 2004).

The reason for the hydrotreating of petroleum fractions is to remove sulfur, nitrogen, oxygen and heavy metals. In VGO, sulfur is present in the form of condensed

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heterocyclic compounds, however, also there is nitrogen in the form of condensed heterocyclic in these fractions. This heteroatom asks for more severe pressure and temperature conditions to be removed (Girgis & Gates, 1991).
Froment et al, (1994) have reported the challenges about the modelling of HDS reactors, associated with the hydrodynamics, but also with the complex nature of the feed. Accounting for the thermodynamic properties of such a mixture is not a simple task, even if the basic data are available or can be estimated. Kinetics is a major element of reactor modeling and simulation, the kinetic aspects of the transformation of the large number of S- and N-components are a formidable problem.
The experimental data used in this work were obtained in a pilot plant from Petroleum Colombian Institute Ecopetrol-ICP. Several types of feedstock such as VGO and Demetalized Oil (DMO) were hydrotreated in a fixed bed reactor. All tests were done with commercial Co-Mo/γ-Al2O3, catalyst. The pilot plant fixed bed reactor is isothermal and up flow.

2. Sequential Design of Experiments

Experimental design is always a problem of optimization concerning to the choice of the experimental conditions in order to maximize the efficiency of experiments with respect to the problem to be solved. The sequential methods take advantage of the information and insight obtained from the previous experiments to select the settings of the independent variables for the next experiment in an optimal way (Froment and Bischoff, 1990). Two types of sequential methods have been developed: for optimal model discrimination and for optimal parameter estimation. The Design Criterion for model discrimination is based upon the divergence and is defined as follow:

$$D(x_u) = \sum_{h=1}^{v} \sigma^{hh} \sum_{r=1}^{m-1} \sum_{s=r+1}^{m} \left| \hat{y}_{uh}^{(r)} - \hat{y}_{uh}^{(s)} \right| \tag{1}$$

where m is the number of rival models and the grid points are numbered u. The setting of operating variables (x) for the nth experiment is that value which maximizes the divergence D(xu). r y s are the rival models, and σhh is a weight factor.
For optimal parameter estimation have been developed several methods, but the most used is the minimum volume design; there the confidence region is represented by a closed hyperellipsoid, where its volume is given by:

$$Volume = C \prod_{j=1}^{p} \sqrt{\frac{\delta}{\lambda_j}} = C \frac{\left(\sqrt{\delta}\right)^p}{\sqrt{\det X^T X}} \tag{2}$$

C is a constant depending upon the dimension p of the space. X is a matrix of partial derivatives, and δ depending upon the probability level and of degrees of freedom.
The next experiment is designed in the grid point where the determinant is maximized.

3. Reactor Model

Two three-phase reactor model reported in the literature were combined and used in the present investigation (Korsten and Hoffman, 1996; Froment et al, 1994). The model

includes correlations for determining oil density, Henry coefficient H_i , solubility of H_2, solubility of H_2S, gas-liquid mass-transfer coefficient, dynamic liquid viscosity, diffusivity D_i, molar volume, liquid-solid mass-transfer coefficient, specific surface area a_S, etc. under the process conditions, using information reported in the literature. (Pooling et al, 2001; Korsten and Hoffman, 1996; Avraam and Vasalos (2003))

The following assumptions were made to the model derivation:

- The main reactions were HDS, HDN and mono-, di- and tri-aromatics HDA
- The reactions occurred in the liquid phase in contact with the catalyst surface
- One dimensional heterogeneous model with both the gas and liquid phase in plug flow and uniform pellet properties were assumed.
- The reactor is concurrent and down flow. No maldistribution, no radial concentration gradients, and the liquid volume in the reactor remains constant.
- The reactor operates adiabatically, so there is no radial transport of heat.
- It was assumed that the external mass transfer would be negligible.
- Catalyst wetting complete, no catalyst deactivation, reaction takes place only at the active catalyst sites. Catalyst, liquid, and gas are in the same temperature
- No evaporation of liquid, and hydrocarbon concentration does not change.

In addition, a suitable numerical package was developed for the evaluation of the thermophysical properties of oil compounds and mixtures and for the detailed calculation of interfacial mass transfer rates. All variables of the system were considered to be functions of (dimensionless) space variable.

We present briefly the main equations comprising the model (nomenclature is given in Korsten and Hoffman, 1996; and Froment et al, 1994). The mass-balance equations for the gaseous components and for the gaseous compounds in the liquid phase are:

$$\frac{u_G}{RT}\frac{dp_i^G}{dz}+k_i^G a_L\left(\frac{p_i^G}{H_i}-C_i^L\right)=0 \tag{3}$$

$$u_L\frac{dC_i^L}{dz}+k_i^L a_L\left(\frac{p_i^G}{H_i}-C_i^L\right)-k_i^S a_S(C_i^L-C_i^S)=0 \tag{4}$$

The mass-balance equation for the sulfur compounds and the liquid hydrocarbon is:

$$u_L\frac{dC_i^L}{dz}+k_i^S a_S(C_i^L-C_i^S)=0 \tag{5}$$

The mass balance for solid phase, and its boundary conditions are:

$$\frac{D_{ie}}{\varepsilon^2}\frac{dC_{is}}{d\varepsilon}\left(\varepsilon^2\frac{dC_{iS}}{d\varepsilon}-C_i^L\right)=\rho_s\sum_{j=1}^{Nr}S[j,i]^*r_j(C_{iS},...,T_S) \tag{6}$$

at $\varepsilon = 0$, $\dfrac{dC_{is}}{d\varepsilon}=0$; and, at $\varepsilon = R$, $K'(C_i^L-C_i^S)=D_e\dfrac{dC_i^S}{dr}$ (7)

4. Kinetic expressions of heterogeneous chemical reaction rates:

4.1 HDS:

The sequential discrimination procedure, supplemented with a statistical analysis of the data, selected a kinetic model out of nine rival models (Broderick and Gates, 1981; Cheng et al, 2001; Cotta et al, 2000; Girgis and Gates, 1991) after a maximum of 8 experiments, 4 of which were designed.

For DBT hydrogenolysis, and DBT hydrogenation:

$$r_{DBT-\sigma} = \frac{k_1 C_{DBT} C_{H2}}{(1 + K_{DBT} C_{DBT} + K_{H2S} C_{H2S})^2 (1 + K_{H2} C_{H2})} \tag{8}$$

$$r_{DBT-\tau} = \frac{k_2 C_{DBT} C_{H2}}{(1 + K_{DBT} C_{DBT})(1 + K_{H2} C_{H2})} \tag{9}$$

4.2 HDN:

The selected kinetic model is (Avraam et al, Cat. Today. 2003)

$$r_{HDN} = \frac{k_3 K_{12} C_N C_{H2}}{(1 + K_{1,H2S} C_{H2S} + K_{1,A} C_A)^2} + \frac{(1 - k_3) K_{22} C_N C_{H2}}{(1 + K_{2,H2S} C_{H2S} + K_{2,A} C_A)^2} \tag{10}$$

4.3 HDA: Based on: $A_1 + \alpha H_2 \Leftrightarrow A_2$

$$r_{HDA} = \frac{K_{H2} C_{A1}}{(1 + K_{1,H2S} C_{H2S})} + \frac{K_D C_{A2}}{(1 + K_{1,H2S} C_{H2S})}, \text{ where} \tag{11}$$

$$K_H = K_{H,0} P_{H2}^x e^{-(E/R)(1/T - 1/T0)} \;\; ; \;\; K_D = \frac{K_{H,0}}{K_P P_{H2}^{\alpha - x}} e^{-(E - \Delta H/R)(1/T - 1/T0)} \tag{12}$$

5. Integration Method

The integration in the axial direction was integrated along the reactor length using a fourth order Runge-Kutta-Gill algorithm with variable step size. The intraparticle integration is a boundary value problem. Orthogonal Collocation Method was used successfully. (Finlayson, 1982; Villadsen and Michelsen, 1978)

6. Experimental

The liquid feed was a typical vacuum gas oil (VGO) obtained from Refinery of Barrancabermeja, Colombia. (20°API, 1.8 wt % sulfur, 1150 wppm total nitrogen, 42.8 wt % total aromatics). Temperature monitoring and control was accomplished via five thermocouples which were placed in a thermowell with an external diameter of 6e-3 m. The range of the operating parameters was: liquid feed rate 8.61e-6 / 9.51e-5 kg/s, hydrogen feed rate 2.5e-6 / 3.56e-5 Nm3/s, temperature 350 – 390°C, total pressure 3 – 7 e6 Pa, LHSV ranged from 0.4 to 3 h-1, gas/oil ratio from 0.1 to 3.0 Nm3/kg.

7. Results

7.1. Operational Variables

The influence of main operational variables used in industrial HDT units and their impact on the reactor performance can be summarized as follow: to improve the sulfur and nitrogen conversion, four procedures can be chosen: increase temperature, decrease space-velocity, increase pressure, or increase reactor length. However to increase the reactor temperature will result in shorter catalyst cycle length. A decrease in space-velocity also will reduce the plant capacity, and, so that new HDT reactors will have to be added in order to maintain the existing production capacity. An increase in hydrogen partial pressure would be favorable for aromatics contents reduction too, but the plants do not allow for an increase of total pressure due to existing physical constraints of maximum pressure, like this to increase the reactor length results impractical. On the other hand, a possible way to deal with the problem is to have a quench, but this problem is outside the scope of this research.

7.2. Effect of aromatics and nitrogen containing compounds

It was found in the present study that the increasing concentration of naphthalene in the feedstock reduced the HDS rates (inhibits both routes -hydrogenolysis and hydrogenation- by a nearly equal percent). Phenanthrene has to be considered too, since a low concentration is enough to decrease significatively the HDS rate.

Usually, nitrogen compounds in oil fractions can be classified into two main chemical classes: basic and non-basic. Alkyl-substituted carbazoles (non-basic) were found in large amounts in the feed, and carbazole compounds substituted at position 1 were found to be the most abundant. Our results confirm the poisoning effect of carbazol (non-basic) and acridine (basic), even at low concentrations. Indicating that partially hydrogenated N-compounds may have a more important effect than the parent structure.

7.3. Modeling of HDT Pilot Plant

After the kinetic parameters were determined, simulations that used only mass-balance equations were performed, because the pilot reactor operates at constant temperature. Three experiments at different temperatures were made, and a comparison between experimental and calculated mass concentrations of sulfur, nitrogen, and aromatics, as a function of reaction temperature show an average absolute error for all predictions is less than 5%. The simulated molar concentration profiles in the reactor, based on the parameters given earlier, are shown in Figure 1.

It is observed that the gradients of concentrations are more or less constant along the reactor, and that the H2S concentration rapidly increases, which is due to the high reaction rate (sulfur removal) of the catalyst bed in the initial part of the reactor.

8. Conclusions

A sequential design of experiments based on sequential quadratic programming was used for model discrimination, and estimate their kinetic parameters from pilot plant data. A typical VGO from Colombian refinery was used like liquid feed. A steady-state heterogeneous model was developed to realize the simulation of HDT pilot plant, where the HDS, HDN and the HDA reactions have been included. The model for solid phase

was solved using Orthogonal Collocation Methods and for liquid and gas phase using Runge Kutta methods.

It was verified the influence of the main operational variables (T, P, LHSV, H2/Oil ratio) in VGO and heaviest loads like Demetalized Oil (DMO) corroborating than high temperature, pressure and H2/Oil ratio, and low LHSV improve the sulfur and nitrogen conversion. Was detected inhibition of HDS reactions with aromatics molecules like naphthalene and phenanthrene, and with basic and non-basic nitrogen compounds like acridine and carbazole. Finally, the agreement between theoretical and experimental data led to the development of a user-friendly interface to facilitate the simulation and its interpretation.

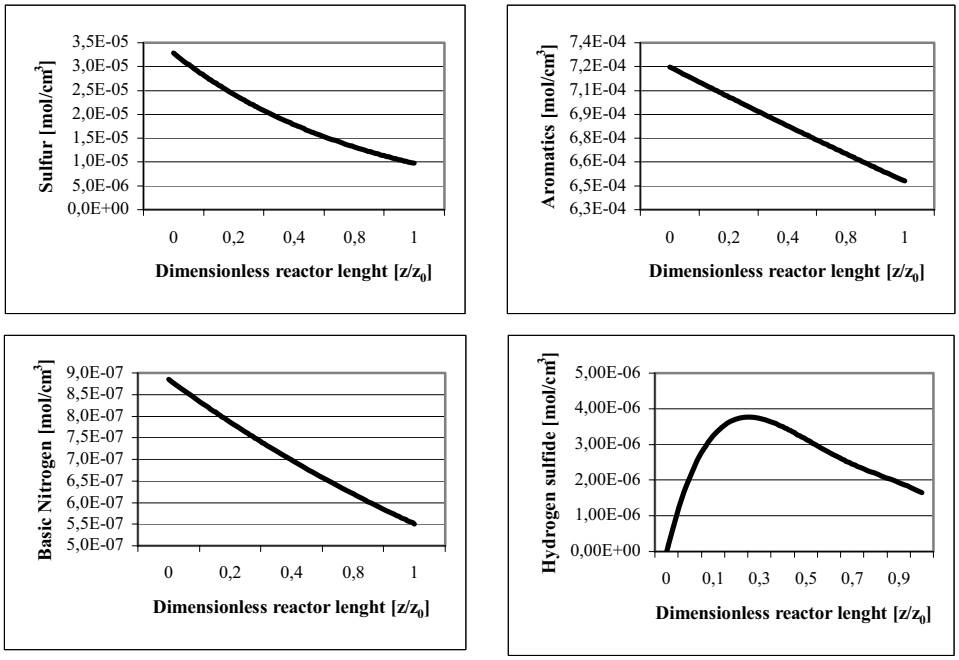

Figure 1. Concentrations of sulfur, aromatics, basic nitrogen and H_2S along the reactor

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