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Modeling of trickle bed reactor for hydrotreating of vacuum gas oils: effect of kinetic type on reactor modeling

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Abstract

The hydrodesulfurization (HDS) processes research requires a lot of experimental work to define promotion and inhibition effects and find out correlations between the variables that participate on the sulphur removal. By means of modeling and simulation is possible to determine the scope of the process, and by means of the sequential design of experiments (SDE) is possible to reduce the experimental work required through comparison of kinetic models, at the same time that it predicts experimental conditions that allow to select a unique model and estimate its parameters. The purpose of this work was to simulate the HDS process using the mathematical model developed in previous work and several kinetic models founded in literature. Together simulation is proposed a SDE-based software with Runge-Kutta routines, orthogonal collocation methods an Sequential Quadratic Programming to develop the steps of the Design and to be used on pilot plant applications. The good agree between theoretical and experimental data led to the development of a user-friendly program to simulate the complex process, make easier the interpretation of simultaneous reactions, and become a useful tool for to improve the operation conditions of hydrotreating industrial reactors.

Keywords

Sequential, experiments, hydrodesulfurization, kinetics, optimization

1. Introduction

To accomplish with the actual legislation and at the same time improve the quality of liquid fuels, it is useful to simulate the petroleum fraction hydrotreating process at different operation conditions. However, it is necessary to carry out series of experimental tests, to study and characterize this process, in order to determine the best operation conditions that allow establishing mathematic correlations between the studied variables. The kinetic is maybe the major element of reactor modeling and simulation, and therefore particular attention must be paid. This work is further development of our research in the area of computer aided modeling for hydrodesulfurization, hydrodenitrogenation and hydrodearomatization simultaneous reactions in a hydrotreating industrial process. In previous work [1] the process model was created by the combination of two multiphase models reported in literature for gas and liquid phase and for solid phase respectively. The main purpose of this work is to compare the behavior of HDT reactions taking into account several kinetic models founded in literature, and apply techniques of SDE in order to select the kinetic model that best represents the HDS process according with the operative conditions suggested by the software itself. A complete review of kinetic models for different petroleum fractions was carried out, likewise comparative analysis for type of processing, type and nature of reacting systems, modes of operation, process conditions, expressions for mass transfer, physico-chemical properties, and numerical methods to solve the respective equations systems was made, and used as a base for carry out new experimentation at pilot plant for hydrotreating of heavy petroleum fractions.

2. Reactor Modeling

For liquid and gas phases the three-phase model reported by Korsten and Hoffman (1996) was combined with the solid phase model reported by Froment et al. (1994). The main assumptions and model simplifications were: reactor model is one-dimensional heterogeneous and operates isothermally, the reactions occur in the liquid phase in contact with the catalyst surface, external mass transfer is negligible, catalyst wetting is complete, there is no catalyst deactivation; and there is no evaporation of liquid
The expressions for estimation of the physico chemical properties (in order to solve the differential equations) were obtained from authors [2-3]. Two different data set of basic information for the simulation, corresponding with reactor geometry (length and diameter), catalyst properties (density, superficial area, equivalent size), inlet operative conditions (temperature, pressure, liquid and gas flows), and inlet concentrations of key components, among others, were selected in order to compare all the kinetic models into the reactor model. The first data set was obtained from industrial information [4] the second data set was obtained from experimental tests made at pilot plant [1]. Both data sets are

presented in Table 1. Finally, a user-friendly computational program was developed based on programming of Matlab 7.0®, which have many tools that allow to apply optimization process and differential equations solutions approximation with a wide range of defined matricial functions. The axial direction in reactor was performed using a fourth order Runge-Kutta routine with variable step size, and the intra-particle integration was carried out with an orthogonal collocation method (second order differential equations).

3. Kinetic Model

To represent the HDS process have been incorporated nine kinetic models (considering the presence of sulphur in form of dibenzotiophene-DBT) established by several authors [4-11]. Some of these models consider two kinetics expressions, one for hydrogenolysis and other for hydrogenation of dibenzothiophene. The selected kinetic models to use in simulation of HDS process are presented in Table 2 (donde r_i = Reaction velocity of "i" component, C_i = Concentration, P_i = Pressure, k_i = Reaction velocity coefficients, K_i = Absorption equilibrium constant.

4. Results

Concentrations profiles for DBT, H_2S and H_2 in liquid and gas phases corresponding with the considered kinetic models were obtained. In Figures 1-4 are shown behaviors for concentration of DBT in liquid phase along reactor (for four kinetic models, two Langmuir-Hinshelwood type and two power law type, like representatives of the other kinetic models), whereas in Figures 5-8 are shown for H_2S. These behaviors are based on data set of industrial information.
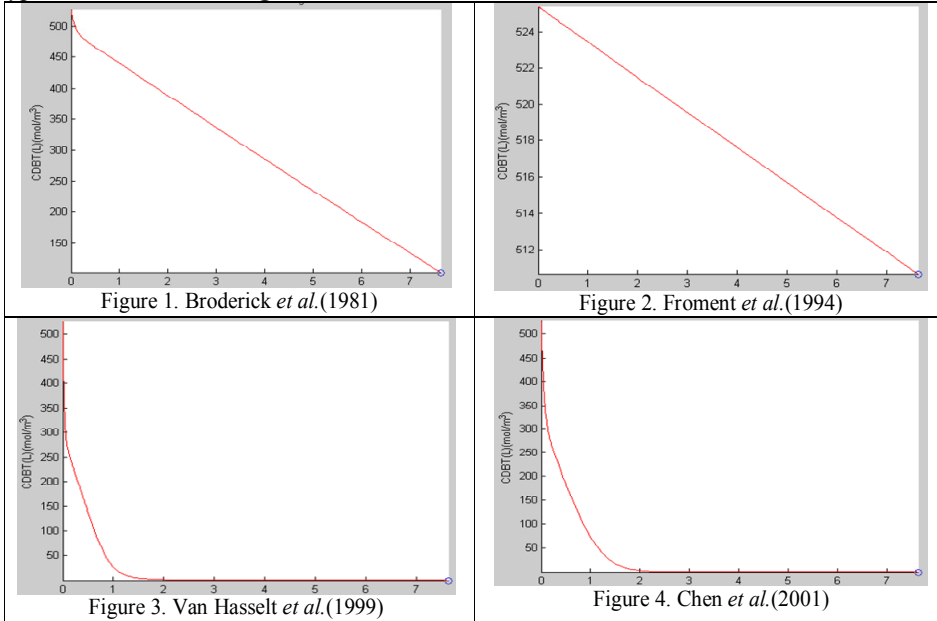
Table 1. Basic data sets for reactor simulations

Property	Value	Property	Value	Propetry	Value	Property	Value
Operation Conditions		Feed Characteristics		Catalyst Characteristics		Inlet Conditions	
Temperature (K)	590*	Liquid Den. (kg/m³)	968.12*	Real Dens. (kg/m³)	1420*	Pressure H₂ (Pa)	3.1e6*
	603.15**		863**		337.8**		9e6**
Pressure (Pa)	5e6*	Reactor Characteristics		Bula Dens. (kg/m³)	710*	Pressure H₂S (Pa)	0*
	9e6**				327.3**		0**
Gás Flow (m³/s)	3.63*	Diameter (m)	2.82*	Particle Diameter (m)	1.3e-3*	DBT Conc. (mol/m³)	525.4*
	2.2e-5**		19e-3**		1.6e-3**		66**
Liquid Flow (m³/s)	2.09e-2*	Lenght (m)	7.62*	Especific Area (m²/m³ᵣ)	8.9e7*	H₂ Conc. (mol/m³)	256*
	1.1e-7**		0.73**		3.6e8**		0**
*Data from Froment *et al.* (1994) **Data from Pilot Plant						H₂S Conc. (mol/m³)	0*
							0**

Table 2. Kinetic models for simulation of HDS process.

Model	Hydrogenolysis	Hydrogenation
1. Girgis and Gates (1991)	$r = \dfrac{k \cdot K_{DBT} \cdot K_{H_2} \cdot C_{DBT} C_{H_2}}{\left(1 + K_{DBT} \cdot C_{DBT} + K_{H_2S} \cdot C_{H_2S}\right)^2 \cdot \left(1 + K_{H_2} \cdot C_{H_2}\right)}$	$r = \dfrac{k' \cdot K'_{DBT} \cdot K'_{H_2} \cdot C_{DBT} \cdot C_{H_2}}{\left(1 + K'_{DBT} \cdot C_{DBT}\right)}$
2. Froment et al (1994)	$r_{DBT-CHB} = \dfrac{k_2 \cdot K_{DBT,\tau} \cdot C_{DBT} \cdot C_{H_2}}{\left(1 + K_{DBT,\tau} \cdot C_{DBT}\right)^3}$	$r_{DBT-BPH} = \dfrac{k_1 \cdot K_{DBT,\sigma} \cdot K_{H_2,\sigma} \cdot C_{DBT} \cdot C_{H_2}}{\left(1 + K_{DBT,\sigma} \cdot C_{DBT} + \sqrt{K_{H_2,\sigma} \cdot C_{H_2}} + K_{H_2S,\sigma} \cdot \dfrac{C_{H_2S}}{C_{H_2}}\right)^3}$
3. Broderick et al (1981)	$r = \dfrac{k \cdot C_{DBT} \cdot C_{H_2}}{\left(1 + K_{DBT} C_{DBT} + K_{H_2S} \cdot C_{H_2S}\right)^2 \cdot \left(1 + K_{H_2} \cdot C_{H_2}\right)}$	$r_{DBT-\tau} = \dfrac{k_2 C_{DBT} C_{H2}}{(1 + K_{DBT} C_{DBT})(1 + K_{H2} C_{H2})}$

4. Avraam-Vasalos (2003)		**5. Chen et al (2001)**
$r_{HDS} = \dfrac{K_{11}^E \cdot C_{H_2}^S \cdot C_{DBT}^S}{\left(1 + K_{H_2S}^{HDS} \cdot C_{H_2S}^S + K_A^{HDS} \cdot C_{DBT}^S\right)^2}$		$r_A = K \cdot C_{DBT}^{1.12} \cdot C_{H_2}^{0.85}$

6. Van Hasselt et al (1999)		**7. Tsamatsoulis and Papayannakos (1998)a**
$r_A = \dfrac{K_r \cdot C_{DBT}^2 \cdot C_{H_2}}{1 + K \cdot C_{H_2S}}$		$r_{HDS} = \dfrac{K_{HDS} \cdot P_{H_2} \cdot C_S^{2.3}}{\left(1 + K_{H2S} \cdot P_{H_2S} + K_{H_2} \cdot P_{H_2}\right)}$

8. Cotta and Maciel-Filho (2000)		**9. Tsamatsoulis and Papayannakos (1998)b**
$r_S = k_S \cdot C_{DBT}^{1.2} \cdot P_{H_2}^{1.5}$		$r_{HDS} = \dfrac{K_{HDS} \cdot P_{H_2}^{2.3} \cdot C_S}{\left(1 + K_{H_2S} \cdot P_{H_2S}\right)}$

There are strong differences on the concentration predicted values along the reactor when are used Langmuir Hinshelwood (L-H) kinetic models with respect to power law (P-L) kinetic models. The formers predict DBT concentrations with a gradual diminution along the reactor whereas the others are in agree with a pronounced reduction of DBT concentration on the first section of the reactor. Is remarkable point out that the employed parameters of this models depends on the specific experimental work conditions (different for most of the models), therefore these differences could result in tendencies and predictions out of established original range. On the other hand, the amount of sulphydric acid (H₂S) on the liquid arises very fast on the first sector of the reactor. Results using L-H kinetic show almost constant production of H₂S along reactor, whereas using P-L kinetic the DBT is consumed very fast and the H₂S diminish to almost zero after the first sector of the reactor. The second data set of basic information (pilot plant) present higher temperature, almost twice the pressure, and some catalytic properties are better for HDT process, related with the first data set. Therefore the concentration profiles (not shown here) result very similar to the presented in Fig.1-8, however the consume of DBT and production of H₂S are very much faster and the slopes more pronounced.

Figure 1. Broderick *et al.*(1981)

Figure 2. Froment *et al.*(1994)

Figure 3. Van Hasselt *et al.*(1999)

Figure 4. Chen *et al.*(2001)

Figures 1-4. Concentrations profiles for DBT (vertical axis) along reactor (horizontal axis)

Figure 5. Broderick *et al.*(1981)

Figure 6. Froment *et al.*(1994)

Figure 7. Van Hasselt *et al.*(1999)

Figure 8. Chen *et al.*(2001)
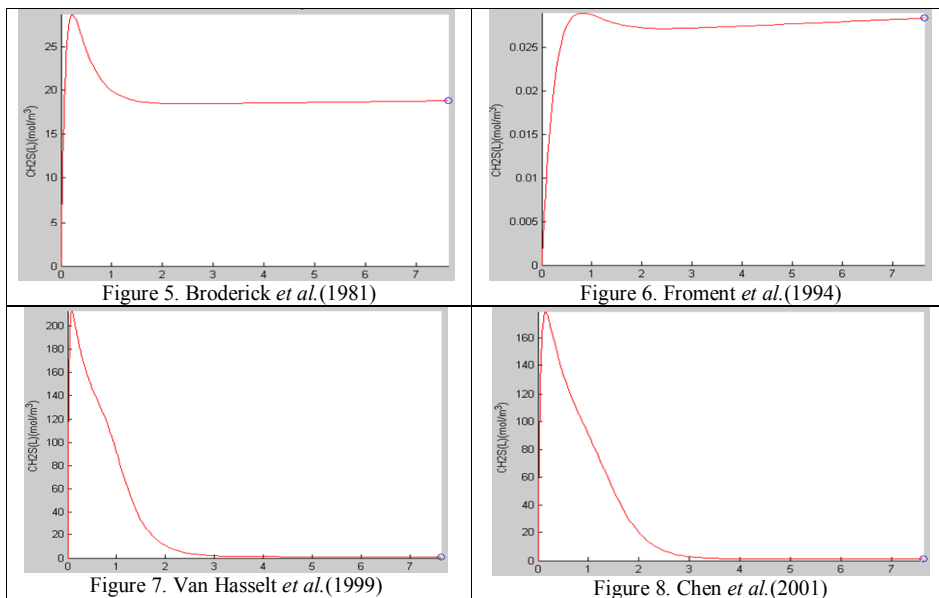
Figures 5-8. Concentrations profiles for H_2S (vertical axis) along reactor (horizontal axis)

On the other hand, it was proposed the use of SDE in order to compare all the kinetic models and to select that which best represent de HDS process over the operative conditions suggested by the software itself. Techniques like Sequential Quadratic Programming (SQP) for each one of the restrained optimization process necessary for the application of criteria of the SDE, Orthogonal Collocation Method for the solution of the second order differential equations, and Runge-Kutta method for the systems of differential equations, were used in the software. For the validation of discrimination of kinetic models were used results reported in literature [12], obtaining the same final kinetic model and estimating parameters in the same order de magnitude with respect to those presented by the authors. Trough a SQP process, it was founded the experimental point where the nine selected kinetic models for HDS process had the maximum difference in their responses. Then, each time some models had to be eliminated until completes the process.

5. Conclusions and future work

Were compared several kinetic models into the modeling and simulation of a trickle bed reactor. It was developed specific software based on Matlab 7.0® for simulation and sequential design of experiments (SDE) and were validated with several papers reported in literature, obtaining results that are in concordance with data and behaviors reported. Also, it was shown that power law kinetic models generate concentration profiles for consume of DBT and production of H_2S very different with respect to Langmuir-Hinshelwood kinetic models, however the software reproduced very well the behaviors for reactive and products with two different data set: industrial and pilot plant information.

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