MODELING AND OPTIMIZATION OF GAS OIL HDS IN TRICKLE BED REACTOR

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Abstract: The present work aims to optimize an industrial HDS process. The chemical process is considered to take place in the three phase catalytic trickle-bed reactor. Non-linear kinetics coupled with transitional mathematical model of the gas, liquid and solid phases are used to describe the dynamic behavior of the multivariable process. Due to the high dimensionality and non-linearity of the kinetic model, the solution of the optimization problem through conventional algorithms does not always lead to the convergence. This fact justifies the use of an evolutionary method, based on GA, to deal with this process. In this way, the GA code is coupled with the rigorous model of the reactor. The aim of this optimization is searching the process conditions and reactor length that maximize the productivity of sulfur content of the outlet oil subject to the environmental constraint of exit sulfur concentration. The results show that GA could successfully converge to the optimal conditions.

Keywords: Mathematical modeling, trickle bed reactor, dynamic simulation, optimization, Genetic algorithm

1. MATHEMATICAL MODEL

The reaction can be described by the following equation: (Korsten et al., 1996)

\[ v_S S_{(\text{liquid})} + v_{H_2} H_{(\text{gas})} \rightarrow v_{HC} H_{C_{(\text{liquid})}} + v_{H_2S} H_{2S_{(\text{gas})}} \]

The exit sulfur concentration should be as low as possible due to severe environmental specifications. In this way, the exit sulfur concentration is defined as a constraint of the process, limited to 100 ppm or even less.

The mathematical model used to describe this process is the one developed by (Fabian S. Mederos, Jorge Ancheyta, 2007). This model includes material balances for the three phases. It neglects the diffusion in the catalyst particles. The following hypotheses were assumed in development of the model:

1. The reactor operates in dynamic condition.
2. Gas and liquid flows are co-current.
3. Gas and liquid velocities are constant through the reactor.
4. Constant density of gas and liquid phases.
5. There are not radial concentration and temperature gradients.
6. Catalyst activity does not change with time.
7. Vaporization and condensation of oil do not take place.
8. Constant pressure.
9. Chemical reactions take place only at the solid catalyst.
10. Mass resistance in the gas side of the gas–liquid interface is assumed to be negligible.
1.1 Mass balance

Mass-balance equations in the TBR (trickle bed reactor) for co-current operations are described with the following set of partial differential equations (PDEs) and ordinary differential equations (ODEs):

**Gas phase**

\[
\frac{\varepsilon_G}{RT_G} \frac{\partial p_i^G}{\partial t} = - \frac{u_G}{RT_G} \frac{\partial p_i^G}{\partial z} - k_i \alpha_i \left( \frac{p_i^G}{H_i} - C_i^L \right)
\]

(1)

Where \( i = \text{H}_2, \text{H}_2\text{S}. \)

**Liquid phase**

\[
\varepsilon_L \frac{\partial C_i^L}{\partial t} = u_L \frac{\partial C_i^L}{\partial z} + \varepsilon_i D_i^e \frac{\partial^2 C_i^L}{\partial z^2} + k_i \alpha_i \left( \frac{p_i^G}{H_i} - C_i^L \right) - k_i \alpha_i \left( C_i^L - C_i^S \right)
\]

(2)

Where \( i = \text{H}_2, \text{H}_2\text{S}. \)

\[
\varepsilon_L \frac{\partial C_i^L}{\partial t} = u_L \frac{\partial C_i^L}{\partial z} + \varepsilon_i D_i^a \frac{\partial^2 C_i^L}{\partial z^2} - k_i \alpha_i \left( C_i^L - C_i^S \right)
\]

(3)

Where \( i = \text{S}, \text{HC}. \)

**Solid phase**

\[
\varepsilon_s (1 - \varepsilon) \frac{\partial C_i^S}{\partial t} = k_i \alpha_i \left( C_i^L - C_i^S \right) \pm \rho_b \varepsilon \eta_{\text{HDS}} r_{\text{HDS}} \left( C_i^S, ..., T_s \right)
\]

(6)

Where \( i = \text{H}_2, \text{H}_2\text{S}, \text{S}, \text{HC}. \) "-" sign is for the reactants, and the "+" sign is for the products. Because the concentration of hydrocarbon is the main component of the feedstock and it does not change significantly during HDS of VGO, Eqns. (3) and (6) for \( i = \text{HC} \) will not be considered in the simulations. More details about reactor parameters, feed specifications, operating conditions and properties of catalyst can be found in Table 1 and 2. (Korsten, 1996).

Since hydro- desulphurization reactions at the usual process conditions are irreversible (Froment et al. 1991), reverse reactions need not be considered. Assuming the sulfur content of the oil and the concentration of hydrogen to have a positive effect, and hydrogen sulfide to adsorbs at the active catalyst sites, the following kinetic equation of the Langmuir-Hinshelwood type is used:

\[
r_{\text{HDS}} = k_{\text{app}} \frac{(c_i^S)^{m_1} (c_i^H)^{m_2}}{(1 + K_4 \varepsilon_{H,S}^2)^2}
\]

(7)

Where the rate of reaction per unit mass of the catalyst is correlated with the concentrations at the outer catalyst surface; \( m_1 \) and \( m_2 \) represent the reaction order concerning the sulfur compound and hydrogen, respectively; \( k_{\text{app}} \) is the apparent rate constant, as discussed below; and the adsorption-equilibrium constant of hydrogen sulfide at the catalyst surface is represented by \( K_4 \).

2. RESULTS AND DISCUSSION

2.1. Interpretation of the model results

Simulation, using the reactor model described in Section 3, was carried out to observe the behavior of co-current mode of operation. Fig. 1 shows the dynamic concentration of the exit sulfur from the
reactor as a function of time for co-current operation. The steady condition of the experimental sulfur concentration is being compared with the model in this figure to a good accuracy.

Fig. 1. Sulfur concentration of the liquid at the bed outlet as a function of time and validation of the model at steady condition.

It is seen that sulfur has zero concentration at the exit of the reactor from zero to about 750 s, after that, concentration starts increasing and finally the steady-condition is achieved at 5000 s. Fig. 2 presents the liquid molar concentration profiles of sulfur along the catalytic bed with co-current downward flow of gas and liquid, at times very close to the beginning of the operation (250 s), intermediate times (1750 s, 3250 s), and when the steady conditions is achieved. At steady condition, the sulfur content in the exit of reactor shows good agreement with experimental value. After validation and confirmation of the HDS process in the trickle bed reactor at transitional and steady conditions, the optimization procedure was performed on the operational conditions.

Fig. 2. Liquid molar concentration profile of sulfur along the catalytic bed at different times.

2.2. Optimization problem

The optimization objective of this work is to find out the appropriate operational conditions at steady state that lead to the highest amount of sulfur removal in presence of the highest space velocity as the best performance of the reactor translated in terms of maximal productivity, by the following objective function:

\[ f(x) = \text{Productivity} = \frac{(C_{S,\text{inlet}} - C_{S,\text{exit}}) \cdot \dot{U}_L}{L} \]  \hspace{1cm} (8)
However, the productivity is deeply dependent on the exit organic sulfur concentration, which should be as low as possible, due to an environmental constraint. In this way, the exit sulfur concentration is defined as a constraint of the process, limited to 100 ppm or even less. Therefore, the single objective constrained optimization problem can be written as:

Maximize: \( f(x) \)

Subject to: model equations (Eqs. (1), (6)),
Exit sulfur concentration\(<100\) ppm (on weight basis),
\( x \) is composed by the input variables which are discussed later.
The postulated optimization problem is solved by GAs.

2.3. Results of optimization

In order to optimize the process, the GA code (Deb et al. 2000) was coupled with the non-linear mathematical model (Eqs.1 and 2). The variable of liquid velocity was dispersed within \( \pm 80\% \) around the commercial liquid condition. The extent of temperature and pressure was disturbed \( \pm 15\% \) around the feed conditions. The variable of reactor length was distributed \( \pm 15\% \) around the tradition industrial value. The mentioned ranges were chosen related to the actual conditions so that these variables could achieve to the values that made physical and practical sense.

Once the variables range was stipulated, the GA optimizer was coupled to the reactor system in order to maximize the productivity with the constraint of exit sulfur concentration in liquid phase less than 100 (ppm). Extensive simulations were performed in order to obtain the maximization of the productivity of organic sulfur subject to the environmental constraint of exit sulfur concentration in liquid phase less than 100 (ppm). The optimal conditions have been obtained by the solution of the model with the GA optimizer in MATLAB 7.0 software. The optimized variables are determined with a productivity of \( 6.3934 \times 10^{-9} \) (kmol m\(^{-3}\) s\(^{-1}\)) and 83.1279 (ppm) exit sulfur concentration in liquid phase from a feed with 20000 ppm. The set of optimized variables are presented in Table 6.

**Table 6. Optimal results**

<table>
<thead>
<tr>
<th>Variables</th>
<th>Optimized value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_l )(cm/sec)</td>
<td>0.0119</td>
</tr>
<tr>
<td>( u_g )(cm/sec)</td>
<td>0.2238</td>
</tr>
<tr>
<td>( T )(°C)</td>
<td>423.33</td>
</tr>
<tr>
<td>( P )(Mpa)</td>
<td>11.36</td>
</tr>
<tr>
<td>( L )(cm)</td>
<td>68.59</td>
</tr>
<tr>
<td>WHSV (hr(^{-1}))</td>
<td>1.3447</td>
</tr>
<tr>
<td><strong>Response:</strong></td>
<td></td>
</tr>
<tr>
<td>Exit sulfur concen.</td>
<td>83.128</td>
</tr>
</tbody>
</table>

Fig. 3. H\(_2\)S profile in gas phase in optimized situation compared with non-optimized condition.
In Fig. 3, it can be observed that the optimized values resulted in a rising H$_2$S partial pressure at the end of the reactor. In Fig. 4, the optimized values led to a higher reaction rate in the initial part of catalyst bed and this higher reaction rate provoked a more increase in the liquid H$_2$S concentration in the initial part of catalyst bed. Also, the optimized situation presented a less H$_2$S concentration than the non-optimized condition beyond the half-part of the reactor due to its improved liquid–gas mass transfer condition.

Fig. 4. H$_2$S profile in liquid phase in optimized situation compared with not optimized situation

The optimal conditions have shown a productivity of $6.3934 \times 10^{-9}$ (kmol of organic sulfur m$^{-3}$ s$^{-1}$) and 83.1279 ppm exit sulfur concentration, although in the non-optimized condition the productivity was $4.088 \times 10^{-9}$ (kmol m$^{-3}$ s$^{-1}$) with the exit sulfur concentration of 473.53 ppm. Comparison of results exhibits an improvement of 56% in the productivity and 82.45% decrease in the exit sulfur concentration at optimized conditions.

3. CONCLUSION

A TBR model for simulating the dynamic behavior of pilot and commercial HDT reactors has been developed in this work. The model is heterogeneous one-dimensional and includes the most important HDT reaction; the HDS reaction. The dynamic model is capable of simulating isothermal mode of operation. Experimental data of HDS of vacuum gas oil were employed for model validation, and the model simulation results agreed reasonably well with experimental ones. Optimization of the operational conditions to approach to the possible lowest sulfur content has been carried out by GA and the results reasonably exhibit the improvement of the productivity and lowering the sulfur content.

REFERENCES