Production Of Ultra Low Sulfur Diesel: Simulation And Software Development

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ABSTRACT
One of the recent challenges in the petroleum refineries is the reduction of sulfur content of gas oil to the new lower limits. The specification for the sulfur content of gas oil has been reduced from 500 ppm to 50 ppm in 2006. At present, the necessity of even deeper desulfurization is being discussed in Europe and the United States. The simulators are useful tools to manage hydrodesulfurization operation and to improve the profitability of the process. In this regard, software was developed to simulate Hydrodesulfurization process (HDS) in trickle bed reactors. The simulation was based on HYSYS environment, in which the HDS reactor model results (based on Fortran codes) were implemented in it through HYSYS Customization Capability. The multiphase reactor was simulated with a one-dimensional heterogeneous model. The reactor model was validated with the pilot data. By the use of simulation results, the effects of some pertinent operating parameters such as reactor temperature and pressure and H₂/oil ratio in gas oil feed on the performance capability of the HDS plant were investigated. Based on these results the optimum operating conditions were determined. The simulation results have been used to estimate the optimum operating conditions for the HDS pilot plant to be operated in RIPI.

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KEYWORDS
Simulation; Multiphase reactors; Heterogeneous models; Gas oil; Hydrodesulfurization.
INTRODUCTION

The presence of sulfurated compounds in crude oil and heavy fractions is an undesirable issue. Sulfur compounds are one of the most important impurities in various petroleum fractions that cause many problems. For example, in the case of fuels they cause environmental pollution, and in the refining and petrochemical industries they poison catalysts. It can lead to corrosibility in oils and lubricants and poisonous emissions such as SO₂ and H₂S when the fuel is burned.

Several processes have been proposed to deal with the problem of removing these compounds. Hydrodesulfurization technique is very effective in sulfur removal from fuel oil, where the molecules that contain sulfur lose that atom by hydrogenation reactions.

The sulfur containing components are converted to H₂S and Hydrocarbons in presence of Hydrogen on solid catalyst. Hydrodesulfurization process is mostly carried out in trickle bed reactors.

There have been reported many works on hydrodesulfurization. Song[1] reviewed both catalyst and process of desulfurization of fuels. Korsten and Hoffman[2] made a model for desulfurization of vacuum gas oil in a trickle bed reactor. The simulation results showed good agreement with experimental data over a wide range of temperature, pressure, space velocity and gas/oil ratio. They used Langmuir–Hinshelwood kinetics for rate equations. Yamada and Goto[3] compared counter-current and co-current operations for hydrodesulfurization.

Chowdhry et al.[4] expanded Korsten’s models and applied it to desulfurization and dearomatization of the diesel oil. Inert particles were put on the catalyst to transfer hydrogen from gas to liquid. Dearomatization reaction and gas liquid mass transfer in nonactive zone were added to Korsten’s model. Simulation results of desulfurization and dearomatization agreed with the experimental data.

Thiophenic components are known to be the most refractory organic sulfur-containing components. Rigorous kinetics for the hydrodesulfurization (HDS) of thiophene and benzo thiophene has already been derived[5,6]. For dibenzothiophene, hydrodesulfurization rate equations have been reported by Broderic and Gates[7] and by Edvinsson and Irandoust[8]. Broderic and Gates[7] neglected the hydrogenation of biphenyl into cyclohexyl benzene, while Edvinsson and Irandoust[8] did not determine the influence of H₂S concentration on the reaction rates.

Recently kinetic modeling of hydrodesulfurization of oil fraction was introduced by Froment et al.[9]. Their work was proceeded by developing rate equations for all reactions in the network for the hydrodesulfurization of dibenzothiophene on the commercial CoMo/Al₂O₃ catalyst by Vanysselberge and Froment[10].

In the present study, a simulation method for hydrodesulfurization of gas oil in trickle bed reactors is presented. The mass balances are described by a reactor model that is based on the two-film theory[2] and the rate of chemical reactions of Hougen-Watson type[10] is being used.

The proposed model is validated by the pilot data. Based on the reactor model, a hydrodesulfurization process is being simulated. In addition, a parametric sensitivity analysis on the process performance being put forward in order to estimate the optimum operating conditions for the HDS reactor and process.

Formulation of mathematical model

Hydrodesulfurization of oil fractions is carried out in a multiphase reactor. There are three phases in reactor: Fixed bed of porous catalyst particles, a Hydrogen gas phase and a liquid phase. Operation of trickle-bed reactors is marked by the simultaneous presence of two phases, a gaseous and a liquid one, flowing over and through a third catalyst solid phase; both streams are cocurrent downflow[11].

Origins of S in diesel depend critically on how it is formulated from the refinery fractions. Sulphur compounds in the lightest products are usually the easiest and cheapest to treat. The operating conditions for desulfurisation of heavy fractions depend crucially on the chemical nature of the sulphur species present figure 1. Removing S from higher molecular weight dibenzothiophenes (DBT) especially those with side chains in hindering positions are some
of the most difficult desulfurization tasks to achieve.

Among thiophenic compounds in petroleum fractions, dibenzothiophene (DBT) and its derivatives are the least reactive sulfur-containing constituents, and are; therefore, the key components in determining hydrotreating process kinetics.[13]

The present study kinetic modeling and simulation of gas oil HDS reactor has been carried out for dibenzothiophen (DBT) as the most sever resisting component against HDS.

In this work the gas phase assumes to be a mixture of hydrogen (H2) and hydrogen sulfide (H2S) and liquid phase consists of gas oil, containing sulfuric compounds of dibenzothiophene (DBT). HDS reactor Simulation is performed on cobalt molybdenum over alumina support (CoMo/Al2O3) catalyst. Gas phase is continuous phase and liquid phase is dispersed, where its stream on the catalyst particles is shaped to laminar form.[12]

The modeling of a fixed bed HDS reactor is presented here. According to the common classification of fixed bed reactor models, one-dimensional heterogeneous model with plug flow model for both gas and liquid phases is being used.

**Reaction network**

The components that take part in catalytic reactions are enumerated as follows:

HDS of DBT involves two parallel routes: (1) hydrogenolysis of the C-S bonds to give biphenyl and (2) hydrogenation of one of the benzenoid rings followed by rapid hydrogenolysis of the C-S bonds to give cyclohexylbenzene.

The general reaction equation is as follows.

\[ \nu_1 (\text{Sulfur compounds}) + \nu_2 (\text{hydrogen}) + \nu_3 (\text{hydrocarbon}) + \nu_4 (\text{hydrogen sulfide}) \]

The corresponding chemical reactions are as presented as:

1. \[ \text{DBT} + 2\text{H}_2 \rightarrow \text{BPH} + \text{H}_2\text{S} \ (\sigma \text{- Site}) \]  
2. \[ \text{DBT} + 5\text{H}_2 \rightarrow \text{CHB} + 3\text{H}_2\text{S} \ (\tau \text{- Site}) \]  
3. \[ \text{BPH} + 3\text{H}_2 \rightarrow \text{CHB} \ (\tau \text{- Site}) \]  
4. \[ \text{CHB} + 3\text{H}_2 \rightarrow \text{BCH} \ (\tau \text{- Site}) \]

It is generally accepted that there exist two types of adsorption sites on the surface of the HDS catalyst, one site on which DBT and its products competitively adsorb and the other site on which H2 adsorbs.[16]

Based on recent studies of G.F.Froment et al. the two different types of active sites include: \( \sigma \)-site for hydrogenolysis and \( \tau \)-sites for hydrogenation. The above reactions constitute a network that its schematics representation is shown in figure 2.[15]
Rate of reaction

Based on the mechanism proposed by Vanrysselberghe and Froment[10], DBT Hydrogenolyzed into BPH and H2S on the σ-sites and in parallel DBT Hydrogenated into THDBT and HHDBT on the τ-sites, followed by hydrogenolysis into CHB and H2S on the σ-sites.

The rate equations for DBT consumption on the σ and τ-sites and for BPH, CHB on τ-sites are written as follows:

\[ r_{DBT,\sigma} = \frac{k_{DBT,\sigma} K_{H,\sigma} K_{DBT}\sigma C_{DBT} C_{H_2}}{(1 + K_{DBT,\sigma} C_{DBT} + K_{H,\sigma} C_{H_2} + K_{DBT,\sigma} C_{H_2} C_{H_2})^2} \]  

(5)

\[ r_{DBT,\tau} = \frac{k_{DBT,\tau} K_{H,\tau} K_{DBT,\tau} C_{DBT} C_{H_2}}{(1 + K_{DBT,\tau} C_{DBT} + K_{H,\tau} C_{H_2} C_{H_2})^2} \]  

(6)

\[ r_{BPH,\tau} = \frac{k_{BPH,\tau} K_{H,\tau} K_{BPH,\tau} C_{BPH} C_{H_2}}{(1 + K_{BPH,\tau} C_{BPH} + K_{H,\tau} C_{H_2})^2} \]  

(7)

\[ r_{CHB,\tau} = \frac{k_{CHB,\tau} K_{H,\tau} K_{CHB,\tau} C_{CHB} C_{H_2}}{(1 + K_{CHB,\tau} C_{CHB} C_{H_2} + K_{H,\tau} C_{H_2})^2} \]  

(8)

The reaction rate parameters are presented in TABLE 1.

Reactor model equations

The Kinetic modeling is based on the two -film theory as shown in figure 3. Since no reactions occur in the gas phase, the mass -balance equations for the gaseous compounds (components 1,2) are:

\[ u_G \frac{d c_i^{G}}{dz} = - K_{L} a_{L} \left( \frac{C_{i}^{G}}{H_i} \right) \quad i = 1,2 \]  

(9)

Where \( H_i = H_i / RT \)

at \( Z = 0 \) \( C_i^{G} = C_i^{G_0} \) \( i = 1,2 \)

No heat exchange with the surroundings of the reactor has to be accounted for, since hydrotreating...
Reactors are operated adiabatically. Three energy equations are considered, one for each phase. The energy transfer between the gas phase and the liquid phase is made up of a conductive heat flux and convective contribution due to the transport of enthalpy by the interphase mass transfer. The Energy equation for gas phase is presented as:

\[ u_G \rho_G C_{PG} \frac{dT_G}{dz} = -h_{L,G} a_L (T_G - T_L) - \sum_{i=1}^{2} N_i a_L C_{Pi,G} (T_G - T_L) \]  

(10)

at \( Z=0 \) \( T_G=T_{G0} \) \( i=1,2 \)

Mass -balance equation for liquid phase is written as:

\[ u_L \frac{dC_i}{dz} = N_i a_L \sum_{i=1}^{4} (1 - \varepsilon_1) \rho C_i v_i t_i^4 \eta_i \ i=1,2,\ldots,6 \]  

(11)

Where \( N_i = K_{LG,i} C_i^{G} / H_i^{L} - C_i^{L} \)  

(12)

at \( Z=0 \) \( C_i^{L} = C_i^{L0} \) \( i=1,2 \)

For liquid -solid heat transfer a convective transfer term is considered. The Energy equation for liquid phase is written as follows:

\[ u_L \rho_L C_{PL} \frac{dT_L}{dz} = \sum_{i=1}^{2} (1 - \varepsilon_1) \rho C_i v_i t_i^4 (-\Delta H_i) + h_{L,G} a_L (T_G - T_L) + \sum_{i=1}^{2} N_i a_L \Delta H_i^{SOL} (T_L) \]  

(13)

at \( Z=0 \) \( T_i=T_{i0} \) \( i=1,2 \)

In this work a mathematical model for the effectiveness factor calculation of HDS catalyst has been developed. The effectiveness factor for each reaction is calculated from the following formula:

\[ \eta_m = \frac{3 R^2 e}{2 R^2} \int_{0}^{R} \int_{0}^{2\pi} \rho_L \rho C_i \eta_m (C_i^{G}, C_i^{L}, T_L) \right] dr \]  

(14)

Where \( R_c \) is the radius of catalysts.

Mass -balance equations inside catalyst pellet is described as:

\[ \frac{D_e}{r} \frac{\partial}{\partial r} (r^2 C_i^{*}) = -\rho_L \sum_{m=1}^{NR} v_{im} \rho_m (C_i^{G}, C_i^{L}, T_L) \ i=1,2,\ldots,6 \]  

(15)

B.C: \( r=R \ C_i^{*} = C_i^{G} \ i= \) components number  

(16)

\[ r=0 \ \frac{\partial C_i}{\partial r} = 0 \ \ NR= \) Number of reaction

The integration in the axial direction was performed using a fourth order Runge-Kutta routine with variable stepsize. The intraparticle integration was carried out with an orthogonal collocation method. Non-linear algebraic equations in catalyst pellets have been solved by orthogonal collocation method and modified Powel dogleg numeric methods[17,18].

### TABLE 2: Physico-chemical properties estimation methods

<table>
<thead>
<tr>
<th>Property</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat transfer coefficient</td>
<td>Chilton-colburn analogy[19][2]</td>
</tr>
<tr>
<td>Henry coefficient</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>[19,20]</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>[19]</td>
</tr>
<tr>
<td>Molecular diffusivity</td>
<td>Tyn-calus correlation [19]</td>
</tr>
<tr>
<td>Critical specific volume</td>
<td>Razi-daubert correlation [21]</td>
</tr>
<tr>
<td>Gas-liquid mass-transfer coefficient</td>
<td>[22]</td>
</tr>
</tbody>
</table>

### The model parameters

The physico-chemical parameters required by the model are introduced in TABLE 2.

### Main assumptions

By formulating the mass transfer equations, the following assumptions are made.

1. The process is operating in steady state condition.
2. Chemical reactions only take place at the catalyst, and not in the gas or in the liquid phase.
3. Wetting efficiency of 100 percent is assumed.
4. There is no temperature difference inside the catalyst pores.
5. There is no radial concentration profile in the reactor.
6. The reactor is non- isothermal.
7. Vaporization and condensation of oil do not take place.

### Model validation

In order to validate the reactor model, the reactor model predictions have been compared with the data obtained from the pilot plant reported by Korsten and Hoffman[3]. The pilot plant characteristics are shown in TABLE 3.

Figure 4 shows the sulfur and \( \text{H}_2\text{S} \) (in liquid phase) concentration profiles along the reactor length predicted from the model and those from pilot data.
TABLE 3: Input data according to pilot plant[2]

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Input data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press., P, Mpa</td>
<td>10</td>
</tr>
<tr>
<td>Temp., T, °C</td>
<td>370</td>
</tr>
<tr>
<td>WHSV, h⁻¹</td>
<td>0.9</td>
</tr>
<tr>
<td>Reactor diameter (cm)</td>
<td>3</td>
</tr>
<tr>
<td>Reactor length packed with catalyst (m)</td>
<td>0.667</td>
</tr>
<tr>
<td>Bed void fraction</td>
<td>0.5</td>
</tr>
<tr>
<td>Particle void fraction</td>
<td>0.6</td>
</tr>
<tr>
<td>Catalyst particle density (kg/m³)</td>
<td>1420</td>
</tr>
<tr>
<td>Catalyst particle diameter (m)</td>
<td>0.013</td>
</tr>
<tr>
<td>Feed API</td>
<td>22.7</td>
</tr>
<tr>
<td>Mean average boiling point of the feed (°C)</td>
<td>451</td>
</tr>
<tr>
<td>Feed molecular weight</td>
<td>420</td>
</tr>
<tr>
<td>Feed density at 15.6°C (kg/m³)</td>
<td>914.6</td>
</tr>
<tr>
<td>Gas flow rate, Qg (m³/hr)</td>
<td>0.004087</td>
</tr>
<tr>
<td>Liquid flow rate, Ql (m³/hr)</td>
<td>0.0001914</td>
</tr>
</tbody>
</table>

The results show a good agreement between the model predictions and the pilot data. Hydrogen concentration profiles along the reactor length in liquid phase for both the model and pilot data are shown in figure 5. Relative error of near 4 -7% is may be seen between the results obtained from the pilot plant and those predicted the model.

Simulations and discussion

The Gas oil hydrotreater processes straight-run atmospheric and vacuum gas oils from the crude unit and cracked atmospheric and vacuum gas oils from the hydrocracker fractionator and delayed coking Units. As a result of hydrotreating, the sulphur compounds are converted to hydrogen sulphide. The feed system includes two independent gas feed module and liquid feed module.

The gas oil stream entering the unit, pre-heated and mixed with hot hydrogen-rich recycle gas stream (The hydrogen system may be once-through or recycle).

This mixture is passed through a fixed bed reactor (trickle-bed), where hydrogenation of the contaminants occurs. The high-pressure hydrogen-rich gas contacts an aqueous amine solution, which absorbs hydrogen sulphide. After purging a portion to maintain hydrogen purity, the remainder of the hydrogen-rich gas, along with make-up hydrogen, is recycled to the reaction vessel for reuse.

The ammonia produced in the reaction vessel will be dissolved in the process water, which is removed as sour water. The liquid hydrocarbon products from the separation stage are routed to a fractionation section for removal of any dissolved gases and fractionation into naphtha/jet and gas oil. The sour gases are sent to the Hydrogen Recovery Unit for further nitrogen and aromatics reduction. The gas oil is sent to storage for eventual blending into the synthetic crude oil.

A simplified Process flowsheet for a stand-alone hydrotreating configuration is shown in figure 6.

The Research Institute of Petroleum Industry (RIPI) has been being involved in HDS technology development for some years. In this regard and in order to get more realistic data and being more familiar with the challenges of HDS plant operation in the pilot scale, a pilot plant has been designed and is being constructed in the RIPI.

The pilot plant simulation was done using...
HYSYS software. The separate Fortran codes written for the reactor simulation were linked to the Hysys environment using the HYSYS Customization tool. The visual basic program interface was used to link Fortran and HYSYS environment as shown in figure 7.

In figure 8 the PFD of the process simulated by HYSYS is shown. The simulation results up to the reactor input data that are calculated by HYSYS, go to the reactor model codes (fortran codes) to calculate the reactor output results. The reactor output results from the fortran codes are transferred to HYSYS via visual Basic environment. Hysys again calculates the results for the entire simulation up to the end of process, in which low sulfur diesel is produced. The gas oil feed data, reactor specifications
and treated gas oil product characteristics are tabulated in TABLE 4.

**Parametric sensitivity analysis**

Based on the HDS pilot plant simulation, parametric sensitivity analysis has been carried out. In this study, the effects of reactor temperature and pressure and H₂/oil ratio of untreated gas oil on the sulfur concentration of hydrogenated products have been considered.

The concentration profiles of DBT, BPH, CHB and BCH along the reactor length are shown in figure 9. It is seen that CHB is the main product of DBT hydrogenation. The concentrations of BPH and BCH products are too low respect to CHB.

The effect of reactor temperature on hydrodesulfurization was studied at the temperature range of 340-400°C and results are presented in figure 10. As it can be seen, at constant pressure and H₂/oil ratio, the product sulfur content decreases as the temperature increases. The decrease of sulfur concentration is rapid up to about 360°C. Beyond this temperature the decreases is very slow.

Effects of pressure on sulfur concentration are
the hydrogenated products is given in figure 12. It is observed that by increasing $H_2$/oil ratio to 55.7, the sulfur concentration decreases, but it increases again by increasing $H_2$/oil ratio. It means that the optimum $H_2$/oil ratio for use in HDS pilot plant would be about 55.7. This trend is like that happened for pressure and could be described like that.

**CONCLUSION**

Deep hydrodesulfurization of gas oil in the trickle bed reactor was simulated using one dimensional heterogeneous reactor model.

Since hydrodesulfurization is strongly limited by hydrogen sulfide the chemical reaction rate is expressed by Hougen-Watson rate equation\[^{[10]}\]. Also as among thiophenic compounds in petroleum fractions, dibenzothiophene (DBT) is the least reactive sulfur-containing constituents, it was selected as the key component in determining hydrotreating process kinetics.

The present study consist of two sections:

1. **Simulating HDS trickle bed reactor**

For this purpose, the suitable reaction rate (Hougen-Watson rate of reactions type) and mathematical model (one dimensional Heterogeneous model for the reactor, the two film theory for kinetic modeling) was selected and solved. The reactor model results were validated with the pilot plant data.
2. Simulation of HDS process

Following RIPI’s experience in HDS, an HDS pilot plant has been designed and is being constructed in the RIPI. The pilot was simulated by HYSYS in this study and the HDS reactor model results were implemented in it through HYSYS customization tool. The operating conditions of the process simulation were considered like those of pilot plant. Based on the simulation, a parametric sensitivity analysis has been carried out. A better performance of the system is achieved by applying a feed with an H2/oil ratio of 55.7.

Increasing the reactor temperature has a major effect on sulfur concentration in treated gas oil. Increasing reactor pressure up to 12 atm, decreases the sulfur concentration to minimum.

**Notation:**

- $\alpha_{L} = \text{Gas-liquid interfacial area per unit reactor volume} \left( \text{m}^2/\text{m}^3 \right)$
- $C_i^G = \text{Molar concentration of } i \text{ in gas bulk} \left( \text{mol/m}^3 \right)$
- $C_i^L = \text{Molar concentration of } i \text{ in liquid bulk} \left( \text{mol/m}^3 \right)$
- $c_p = \text{Specific heat} \left( \text{kJ/kg°C} \right)$
- $C_{i, s} = \text{Component } i \text{ concentration on the catalyst surface}$
- $FBP = \text{Final boiling point}$
- $H = \text{liquid-gas heat transfer coefficient} \left( \text{W/m}^2\text{K} \right)$
- $H' = \text{Henry’s law coefficient} \left( \text{mol/L atm} \right)$
- $\Delta H_{sol} = \text{Heat of solution (J/mol)}$
- $\Delta H = \text{Heat of reaction (J/mol)}$
- $IBP = \text{Initial boiling point}$
- $k_L = \text{Overall mass transfer coefficient in gas-liquid interface} \left( \text{m}^3/\text{m}^2\text{s} \right)$
- $MeABP = \text{Mean average boiling point of the feed}$
- $N_j = \text{Rate of transfer of } i \text{ from the gas bulk to the liquid bulk} \left( \text{mol/m}^3\text{s} \right)$
- $NC = \text{Number of Component}$
- $R_g = \text{gas constant} \left( \text{kJ/kmol·K} \right)$
- $r_j = \text{rate of reaction } j \text{ per unit catalyst mass for heterogeneous reaction} \left( \text{mol/kg}_{\text{cat}}\text{·s} \right)$
- $T = \text{Absolute temperature (°C)}$
- $u_G = \text{Superficial gas velocity} \left( \text{m/s} \right)$
- $u_L = \text{Superficial liquid velocity} \left( \text{m/s} \right)$
- $\text{WHSV} = \text{Weight hourly space velocity (h}\text{⁻¹)}$

**Greek Symbols:**

- $\sigma = \text{hydrogenolysis site}$
- $\varepsilon = \text{Internal catalyst pore}$
- $\varepsilon_1 = \text{Catalyst bed void fraction} \left( \text{m}^3/\text{m}^3 \right)$
- $\eta_j = \text{Effectiveness factor of reaction } j$
- $\rho_g = \text{Gas density} \left( \text{kg/m}^3 \right)$
- $\rho_c = \text{Catalyst density} \left( \text{kg/m}^3 \right)$
- $u_i = \text{ij component from stociometry coefficient matrix}$
- $\tau = \text{Hydrogenation site}$

**Subscripts:**

- $BCH = \text{bicyclohexyl}$
- $BPH = \text{biphenyl}$
- $CHB = \text{cyclohexylbenzene}$
- $DBT = \text{dibenzothiophene}$
- $H = \text{atomic hydrogen}$
- $H_2 = \text{molecular hydrogen}$
- $H_2S = \text{hydrogen sulfide}$
- $\sigma = \text{With respect to the hydrogenolysis function}$
- $\tau = \text{With respect to the hydrogenation function}$

**Superscripts:**

- $g = \text{gas}$
- $l = \text{liquid}$
- $s = \text{solid}$

**REFERENCES**