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Development of Kinetic and Process Model for Oxidative Desulphurization of Light Fuel using Experiments and Parameter Estimation Technique

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Abstract

The oxidative desulphurization (ODS) of light gas oil (LGO) is investigated with an in-house designed cobalt oxide loaded on alumina ($\gamma$-Al$_2$O$_3$) catalyst in the presence of air as oxidizing agent under moderate operating conditions (temperature from 403 to 473 K, LHSV from 1 to 3 hr$^{-1}$, initial concentration from 500 to 1000 ppm). Incipient Wetness Impregnation method (IWI) of cobalt oxide over gamma alumina (2% Co$_3$O$_4$/γ-Al$_2$O$_3$) is used for the preparation of the catalyst. The optimal design of experiments is studied to evaluate the effects of a number of process variables namely temperature, liquid hourly space velocity (LHSV) and concentration of dibenzothiophene and their optimal values were found to be 473 K, 1hr$^{-1}$ and 1000 ppm respectively. For conversion dibenzothiophene to sulphone and sulphoxide, the results indicates that the Incipient Wetness Impregnation (IWI) is suitable to prepare this type of the catalyst. Based on the experiments, mathematical models that represent a three phase reactor for describing the behavior of the ODS process are developed.

In order to develop a useful model for simulation, control, design and scale-up of the oxidation process, accurate evaluation of important process parameters such as reaction rate parameters is absolutely essential. For this purpose, the parameter estimation technique available in gPROMS (general Process Modelling System) software is employed in this work. With the estimated process parameters further simulations of the process is carried out and the concentration profiles of dibenzothiophene within the reactor are generated.

Key words: ODS, Trickle bed reactor, Mathematical model, Kinetic parameter technique
1. Introduction

Sulphur compounds (mainly, benzo thiophene (BT), dibenzothiophene (DBT) and its derivatives) in oil (fuels) are the main source of air pollution, due to generation of sulphuroxides by the combustion process leading to acid rain. The traditional mode of removal of sulphur in fuels is by catalytic hydrodesulphurization (HDS), commonly known as hydrotreating, and requires modified catalyst and severe operating conditions (temperature, pressure, etc.). This makes the hydrotreating process more expensive compared to other processes\textsuperscript{1,3}. Thiophene compound and its aromatic compounds are the main sulphur components found in the oil feedstock. Sulphur decreasing in the fuel has gained significance owing to increasing awareness about the serious consequences of burning sulphur-bearing fuels. The U.S. Environmental Protection Agency (EPA) had constituted new sulphur standards of diesel fuels and gasoline.\textsuperscript{1}

Oxidative desulphurization (ODS) process is regarded as one of the most promising alternative deep desulphurization operations to get ultra-low sulphur fuels.\textsuperscript{1,4,5} The ODS process of sulphur compounds such as, thiophene (Th), benzo thiophene (BT), dibenzothiophene (DBT) and their compounds are investigated by employing various solid catalysts like Mo-Al\textsubscript{2}O\textsubscript{3},\textsuperscript{6,7} Cobalt–aluminium phosphate\textsuperscript{8}, where the sulphur components are oxidized into their corresponding sulfoxides and sulphones. The greatest advantage of ODS in comparison to HDS process is that the ODS can be conducted in a liquid phase under moderate conditions.

In Oxidative desulphurization reactions, the sulphur compound is oxidized via adding oxygen molecules to form the hexavalent sulphur of sulphones.\textsuperscript{9}

The idea of ODS is actually quite simple. Sulphur compounds are known to be slightly more polar than hydrocarbons of similar structure\textsuperscript{10,11}. However, oxidized sulphur compounds such as sulphones or sulfoxides are substantially more polar than unoxidised sulphur compounds. This permits the selective removal of sulphur compounds from hydrocarbon by a combination process of selective oxidation and solvent extraction or solid adsorption\textsuperscript{12}. Before 1980, the most popular oxidants in the study of ODS are nitric acid and nitrogen oxides and used largely because they have double effects of oxidizing sulphur compounds and nitrating the aromatic compounds to form nitro aromatics with high cetane numbers. However, it has major drawbacks such as poor selectivity, low yield and loss of heating value of the treated oil\textsuperscript{12,13}. Other types of oxidants have also been used, including H\textsubscript{2}O\textsubscript{2}/AcOH, H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}SO\textsubscript{4}, O\textsubscript{3}, KMnO\textsubscript{4} and BuOOH\textsuperscript{14,15,16}, oxygen\textsuperscript{17} and O\textsubscript{2}/aldehyde/cobalt catalysts\textsuperscript{18}.
Three phase reactors with fixed bed of catalyst and co-current down flow of gas and liquid, are utilized widely in different oil, petrochemical and chemical industries besides water industries treating wastewater. Understanding the phenomena that govern the performance of three-phase reactors has played a significant role in designing of such equipment. The hydrodynamic factors such as pressure drop, liquid hold up and catalyst wetting efficiency together with characterization of reaction kinetics as well as transport in catalyst particles are all-important and should to be considered for developing an accurate model of the process. Plug flow model for the liquid phase with modified external liquid holdup, external contacting catalyst effectiveness parameters have been suggested by several investigators in the past. Based on experimental studies with an in-house designed catalyst, the aim of this study is to develop kinetic models for the ODS process. For this purpose, a full process model available in the public domain is used and the reaction parameters of the model are determined by minimizing (optimization) sum of the squared error between the data obtained experimentally and those predicted by the model. The modeling, simulation and optimization process of ODS operation are carried out employing gPROMS software.

2. Experimental Work

2.1 Feedstock (Light Gas Oil)
Light gas oil (LGO), the feedstock used in this study, is provided by the North Refineries (Iraq) with the following specifications: 0.851 sp.gr, 4.9 cSt viscosity at 293K, 55°C flash point, 9.8 ppm total sulphur, 52 cetane index and -39°C pour point, which are tested in North Refineries Company laboratories.

2.2 Dibenzothiophene (DBT)
The dibenzothiophene (DBT) obtained from Aldrich is chosen to study the reactivity of sulphur in the oxidation reaction. Purity of sulphur compound is about 98%.

2.3 Air
Air gas is used as oxidant agent. Oxygen contained in air can be oxidant to sulphur compounds.

2.4 Catalyst
Chemical compounds are used for catalyst preparation, as follow:

2.4.1 Active compound used in the catalyst preparation
Specifications of the active compound used in the catalyst preparation are shown in Table 1 below.
### Table 1: List of chemicals and materials used for catalyst preparation and Aluminum oxide specifications

<table>
<thead>
<tr>
<th>Chemicals and Materials</th>
<th>Purity %</th>
<th>Function</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt nitrate</td>
<td>99.5</td>
<td>Active material</td>
<td>Alpha chemica</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$.6H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deionized water</td>
<td>-</td>
<td>Solvent of active material</td>
<td>Samarra company</td>
</tr>
</tbody>
</table>

#### Aluminum oxide($\gamma$-Al$_2$O$_3$) specifications

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pore volume ($\text{cm}^3/\text{g}$)</th>
<th>Bulk density ($\text{g/cm}^3$)</th>
<th>Surface area ($\text{m}^2/\text{g}$)</th>
<th>Particle diameter (mm)</th>
<th>Particle shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>0.5367</td>
<td>0.671</td>
<td>289</td>
<td>1.6</td>
<td>Sphere</td>
</tr>
</tbody>
</table>

#### 2.4.2 Supported alumina oxide ($\gamma$-Al$_2$O$_3$)

The specification of a commercial spherical particle alumina oxide -type gamma alumina ($\gamma$) is also presented in Table 1, which has been used as a carrier in the manufacturing of catalyst.

#### 2.5 Catalyst Preparation used in Experimental Work

The cobalt solution (Cobalt nitrate) supported on alumina ($\gamma$-Al$_2$O$_3$) has been obtained by IWI method. The preparation procedure is as follows: firstly, 100 gm of the alumina dries in the furnace at 393K for 4 hour for removing the moisture from alumina before impregnation. Secondly, 2.1 gm of cobalt nitrate is added to 40 cm$^3$ deionized water (pore volume of gamma alumina equal to deionized water volume), while the solution is being stirred (using magnetic stirrer) for one hour at room temperature. The pretreated gamma alumina in step one is then transferred into a flask under vacuum (utilizing vacuum pump) for removing gases out of support pores. After that, the solution obtained in the second step is added to gamma alumina with 15-20 drop/min rating and continuous stirring until impregnation of all the solution is complete. The temperature is kept constant at 373 K using a bath water. The impregnated gamma alumina is then left to dry overnight in the furnace at 393K. The aim of this step is to eliminate water. The calcination step is then applied for five
hours in the furnace at 823 K with air. This step converts the metal salts deposited on the \( \gamma \)-\( \text{Al}_2\text{O}_3 \) into metal oxides allowing deposition of active metal oxides on the catalyst support and thus desired physical and chemical specifications of the catalyst are achieved. Calcination step is conducted in **Fertilizer/Northern Company**-Baiji. Figure 1 illustrates the steps and sequence of activities in the catalyst preparation.

### 2.6 Oxidation Operation in Trickle Bed Reactor

#### 2.6.1 Apparatus and Procedure

The experiments are carried out at high temperature and pressure in a trickle bed reactor (TBR) reactor available in Tikrit University (Iraq). TBRs are extensively utilized in oil refineries and the process flow diagram of this system is presented in Figure 2. Three phases existing in such systems are: solid phase (catalyst bed), gas phase (air) and liquid phase (LGO). The continuous oxidation of LGO is carried out in the TBR where the LGO and air are fed in co-current mode. The reactor is made of stainless steel with inside diameter of 1.6 cm and length of 77 cm. Four steel-jacket heaters of equal length are used to control the reactor temperature. The top and bottom (30 to 35 % by volume at each end) parts of the reactor are filled with inert particles to serve as disengaging part. The inner part (40% vol.) of the reactor contains a packing of cobalt oxide catalyst. The LGO is pumped at pressure up to 20 bar with flow rates from 0.0 to 1.65 l/hr. The oxidant gas (air) flows from an air compressor at high pressure and fixed operation pressure is maintained. The LGO with varying DBT concentration is mixed with air before feeding into to the reactor at the desired temperature allowing DBT to oxidize to sulphones. The outlet from the reactor flows through a heat exchanger to high-pressure gas-liquid separator in order to separate excess air from the treated LGO. The description and specifications of the experimental equipment can be found in Nawaf et al.

#### 2.6.2 Experimental Runs

The effect of operational parameters on the reactor performance of ODS using cobalt oxide (\( \text{Co}_3\text{O}_4/\gamma \)-\( \text{Al}_2\text{O}_3 \)) catalyst is evaluated by varying temperature between 403 and 473K and liquid hourly space velocity (LHSV) between 1 - 3 hr\(^{-1}\). The concentration of dibenzothiophene is varied between 500 and 1000 ppm. The oxidation experiments have been conducted in a trickle bed reactor packed with 40% catalyst particles at isothermal condition. The model light gas oil is prepared by adding of DBT to hydro-treated light gas oil (containing 2 ppm of DBT) with specified initial concentrations of DBT. The temperature of the LGO feed tank is controlled using a cooling jacket where the coolant side temperature is maintained below 293K for preventing vaporization of light compounds found in light gas oil. To prevent leaks and to remove any gases
and liquid remained from the last run. Nitrogen gas is passed through the reactor. LGO mixed with air is then passed through the reactor at 2-bar pressure and temperature controller is set to the desired feed temperature. When the air temperature reaches feed injection temperature the dosing pump is turned on to allow a certain light gas oil flow rate and the temperature is raised at the rate of 293K per hour until steady state temperature is reached. At the end of a run, the LGO dosing pump is turned off keeping air gas flow on to backwash any remaining light gas oil. Finally, the air valve is shutoff.

### 2.6.3 Sulphur Measurements (GC-capillary Chromatography)
Dibenzothiophene concentration in feed and product are evaluated according to GC-capillary chromatography. The detailed specifications of the GC-capillary chromatography is given in Naef et al. 38

### 3. Mathematical Model of TBR for ODS Reaction
Process model plays a very important role in industries from operator training, health and safety to design, operation and control. Several investigators have suggested that pore diffusion should be considered within the reaction rate constant (multiplying intrinsic rate constant by effectiveness factor) resulting in a pseudo homogeneous basic plug flow model which is adequate for describing the progress of chemical reactions in the liquid phase of a trickle bed reactor. 20,24,25

### 3.1 Mass Balance Equations
Figure 3 shows a typical TBR with various features (assumption, operation parameters, software used, etc.). The general mass balance for a reactor can be described as:

\[ \text{Mass In} = \text{Mass Out} + \text{Mass Disappearance/Appearance by chemical reaction} + \text{Accumulation} \quad (1) \]

Input of DBT, moles / time = \( F_{DBT} \), Output of DBT moles / time = \( F_{DBT} + dF_{DBT} \), Disappearance of DBT by reaction moles / time = \( (-r_{DBT})dV \), Accumulation of dibenzothiophene = 0

\[ F_{DBT} = (F_{DBT} + dF_{DBT}) + (-r_{DBT})dV \quad (2) \]

\[ dF_{DBT} = d[F_{DBT}(1-X_{DBT})] = - F_{DBT}dX_{DBT} \quad (3) \]

Since \( F_{DBT} = C_{DBT}v_L \), Where \( C_{DBT} \) concentration of dibenzothiophene, moles / volume

\( v_L \) is the volumetric flow rate, volume /time, We obtain on replacement:

\[ F_{DBT0}dX_{DBT} = (-r_{DBT})dV \quad (4) \]
The equation above accounts for DBT compound in the differential part of catalyst vol. \((dV)\). For the catalytic reactor as a whole, the term should be integrated. Now \(F_{DBT0}\), the feed rate, is fixed, but \((-r_{DBT})\) certainly depends on the concentration or conversion of materials.

\[
\tau = C_{DBT0} \int_0^{X_{DBTf}} \frac{dX_{DBT}}{-r_{DBT}}
\]

\((5)\)

### 3.2 Chemical Reaction Rate

Kinetic models are essential for catalyst testing at laboratory scale and for comparing various catalysts for a given task such as ODS. Amongst various methods, parameter estimation technique is one of them where a kinetic model is assumed but its parameters are adjusted by comparing the model predictions with the experimental observations.\(^{26}\) To appreciate the complexity of the chemical reaction one should start with an \(n\)-th order kinetics:

\[
-r_{DBT} = -\frac{dc_{DBT}}{dt} = K_{app}c_{DBT}^n
\]

\((6)\)

Apparent kinetics are relating with the intrinsic kinetics regarding internal diffusion and trickle bed reactor hydrodynamic influences as follows:\(^{27}\)

\[
K_{app} = \eta_0 \eta_{ce} K_{in}
\]

\((7)\)

Where, internal diffusion is described by the catalyst effectiveness factor \((\eta_0)\) and the hydrodynamics by the external catalyst wetting efficiency \((\eta_{ce})\). The chemical reaction is produced as:

\[
-r_{DBT} = -\frac{dc_{DBT}}{dt} = K_{in} \eta_0 \eta_{ce} c_{DBT}^n
\]

\((8)\)

Reaction rate constant for ODS reaction \((K_{in})\) can be estimated for each reaction utilizing the Arrhenius equation as follows:

\[
K_{in} = K_0 e^{\frac{-EA}{RT}}
\]

\((9)\)

\(K_0\) is the frequency or pre-exponential factor and \((EA)\) is the activation energy of the reaction. This term fits experiment well over wide temperature ranges and is highly proposed from different standpoints as being a very good approximation to the actual temperature dependency. The chemical reaction rate can be expressed as:

\[
-r_{DBT} = -\frac{dc_{DBT}}{dt} = K_0 e^{\frac{-EA}{RT}} \eta_0 \eta_{ce} c_{DBT}^n
\]

\((10)\)

If the catalytic reaction of dibenzothiophene oxidation obey \(n\)-th-order kinetic can be integrated and get final expression:
\[ \frac{1}{n-1} \left[ \frac{1}{c_{DBTf}^{n-1}} - \frac{1}{c_{DBT0}^{n-1}} \right] = \frac{k_{app}}{LHSV} \]  \hspace{1cm} (11)

3.3 Reactor Description

The TBR includes a number of control variables: mass transfer coefficients, viscosity and density of the oil, diffusivities, effectiveness factor and others. These factors are evaluated utilizing the relations presented in the literature as follows. For accounting into hydrodynamics and other physical impacts, an apparent kinetic constant can be stated: \( K_{app} = K_{in} f \) (hydrodynamics) and is rewritten as (note that \( \eta_0 \) is employed instead of \( K_{app} \)):

\[ \frac{1}{n-1} \left[ \frac{1}{c_{DBTf}^{n-1}} - \frac{1}{c_{DBT0}^{n-1}} \right] = \frac{\eta_0 \eta_c K_{in}}{LHSV} \]  \hspace{1cm} (12)

The effectiveness factor (\( \eta_0 \)) is to be calculated as function of Thiele modulus (\( \Phi \)) with the following correlations employed for sphere particles: 28

\[ \eta_0 = \frac{3(\phi \coth \phi - 1)}{\phi^2} \]  \hspace{1cm} (13)

Generally, Thiele modulus (\( \Phi \)) for \( n \)-th order irreversible reaction is as follows: 24

\[ \Phi = \frac{V_p}{S_p} \sqrt{\left( \frac{\pi+1}{2} \right) \frac{K_{in} (c_{DBT})^{n-1} \rho_p}{D_{el}}} \]  \hspace{1cm} (14)

\[ \rho_p = \frac{\rho_B}{1 - \epsilon_B} \]  \hspace{1cm} (15)

The effective diffusivity (\( D_{el} \)), where the structure (porosity and tortuosity) of the pore network inside the particle is taken into account through the modeling: 29

\[ D_{el} = \frac{\epsilon_s}{\tau} \frac{1}{D_{mi} + D_{ki}} \]  \hspace{1cm} (16)

Catalyst porosity (\( \epsilon_s \)) can be estimated with the following relation based on experiments of total pore volume (\( V_g \)):

\[ \epsilon_s = \rho_p V_g \]  \hspace{1cm} (17)

The effective diffusivity depends on Knudsen diffusivity \( D_{ki} \) and molecular diffusivity \( D_{mi} \) which can be evaluated as follows: 32, 31, 30

\[ D_{ki} = 9700 \gamma_g \left( \frac{T \gamma}{MW_i} \right)^{0.5} \]  \hspace{1cm} (18)

\textbf{Tyn-Calus} correlation:
\[ D_{mt} = 8.93 \times 10^{-8} \frac{x_L^{0.267} T}{v_{DBT}^{0.443} \mu_u} \]  

(19)

The molar volume of light gas oil (L), can be calculated by the following equation:

\[ v_{DBT} = 0.285(v_{cDBT})^{1.048} \]  

(20)

The critical specific volume of light gas oil (liquid) can be evaluated by a Riazi–Daubert equation:  

\[ V_L = 0.285(v_{cL})^{1.048} \]  

(21)

\[ v_{cL} = (7.5214 \times 10^{-3}(T_{meABP})^{0.2896}(\rho_{15})^{-0.7666})MW_L \]  

(22)

Mean pore radius \( r_g \):

\[ r_g = \frac{2v_g}{s_g} \]  

(23)

The tortuosity factor \( \xi \) of the pore structure, in equation (16) is given by:

\[ \frac{1}{\xi} = \frac{\varepsilon_s}{1 - \frac{1}{2}\log(\varepsilon_s)} \]  

(24)

The external catalyst wetting efficiency of the surface \( \eta_{ce} \), is determined at atmosphere pressure utilizing the equation of Al-Dahhan and Dudukovic.  

\[ \eta_{ce} = 1.617 Re_L^{0.146} Ga_L^{-0.071} \]  

(25)

Reynolds number:

\[ Re_L = \frac{\rho_L u_L d_p}{\mu_L} \]  

(26)

Modified Reynolds number is introduced as:

\[ Re_L^* = \frac{\rho_L u_L d_p}{\mu_L(1-\varepsilon_B)} \]  

(27)

Galileo number:

\[ Ga_L = \frac{d_p^3 \rho_L^2 g \varepsilon_B^2}{\mu_L^2} \]  

(28)

Modified Galileo number:

\[ Ga_L^* = \frac{d_p^3 \rho_L^2 g \varepsilon_B^2}{\mu_L^2(1-\varepsilon_B)^3} \]  

(29)

Bed porosity (bed void fraction) for undiluted catalyst bed may be evaluated utilizing the equations reported by Froment and Bischoff, and introduced by Jarullah et al.:  

\[ \varepsilon_B = 0.38 + 0.073 \left(1 + \left(\frac{d_L}{d_{pe}}\right)^3\right) \]  

(30)
Catalyst bed porosity, equivalent particle diameter ($d_{pe}$), defined as the diameter of a sphere that has the same external surface (or volume) as the actual catalyst particle, which is a sufficient particle characteristic depending upon the particle shape and size.

$$d_{pe} = d_p = 1.6 \text{ mm}$$  \hspace{1cm} (31)

Where ($V_P$) external volume and ($S_P$) catalyst surface. The external volume and surface of regular shape (spherical) can be estimated as:

$$V_P = \frac{4}{3}\pi (r_p)^3$$  \hspace{1cm} (32)

$$S_P = 4\pi (r_p)^2$$  \hspace{1cm} (33)

The LGO density ($\rho_L$) as a function of process conditions is calculated by the Standing-Katz correlation:

$$\rho_L = \rho_o + \Delta \rho_p - \Delta \rho_T$$  \hspace{1cm} (34)

$$\Delta \rho_p = (0.167 + 16.181 \times 10^{-0.0425\rho_o}) \left( \frac{p}{1000} \right) - 0.01 \times (0.299 + 263 \times 10^{-0.0603\rho_o}) \left( \frac{p}{1000} \right)^2$$  \hspace{1cm} (35)

The temperature employed for equation of the liquid density in this relation:

$$\Delta \rho_T = (0.0133 + 152.4(\rho_o + \Delta \rho_p)^{-2.45})(T - 520) \left( 8.1 \times 10^{-6} - 0.0622 \times 10^{-0.764(\rho_o + \Delta \rho_p)} \right)$$

$$(T - 520)^2$$  \hspace{1cm} (36)

**Glaso's** correlation has utilized as a generalized correlation for oil viscosity, as follows: \cite{36}

$$\mu_L = 3.141 \times 10^{10}(T - 460)^{-3.444[\log_{10} API]^a}$$  \hspace{1cm} (37)

$$a = 10.313[\log_{10}(T - 460)] - 36.447$$  \hspace{1cm} (38)

The ($API$) is shown in this equation:

$$API = \frac{141.5}{Sp.gr_{15.6}} - 131.5$$  \hspace{1cm} (39)

The set of equations from 1 to 39 were coded and solved simultaneously using the gPROMS. \cite{21}

4. Parameter Estimation Techniques

Accurate determination of process parameters is essential to benefit from any model-based activities such as design, control, scale-up, etc. \cite{32,37} Evaluation of reaction rate parameters can be accomplished via parameter estimation technique based on experimental data and model predictions so that errors between experimental and predicted data are minimized. The experimental data of the ODS process considered in this work were matched against a simple power law kinetic model (equation 8):
\[ -r_{DBT} = -\frac{dc_{DBT}}{dt} = K_{in} \theta_{in} c_{DBT}^{n} \]

Calculated yields have estimated by integration of equation 8, where \( C_{DBT0} \) is the feed concentration of DBT:

\[
c_{DBT}^{calc} = \left( \frac{c_{DBT0}^{n} LHSV}{c_{DBT0}^{n} LHSV + n \times K_{in} \times (n-1) \times \Delta t} \right)^{1/(n-1)} \]  

(40)

Where, \( C_{DBT}^{calc} \) is the product concentration of DBT, LHSV and \( n \) the reaction order. For parameter estimation, the objective function, \( OBJ \), as presented below, has minimized:

\[
OBJ = \sum_{n=1}^{N_t} (c_{DBT}^{meas} - c_{DBT}^{pred})^2 
\]

(41)

In Eq. (41), \( N_t, C_{DBT}^{meas} \) and \( C_{DBT}^{pred} \) are the numbers of test runs, the evaluated product yield and the predicted one by model, respectively. Using the kinetic parameters reported in the literature (without optimization), the composition of all fractions was estimated via application of model correlations in gPROMS. The comparison between experimental and predicted results using the kinetic parameters published in the literature (without the optimization) is listed in Table 2. As shown in this Table, there is a big variation between estimated and experimental values; therefore, optimization is employed on model variables for minimizing this variation.

4.1 Optimization Problem Formulation for Parameter Evaluation

The parameter evaluation problem formulation is described as follows:

**Given**  
The reactor configuration, the catalyst, the feedstock, the operation conditions

**Optimize**  
The reaction orders of ODS \((n_j)\), reaction constants \((k_i)\) at various temperatures (403, 443, 473, respectively).

**So as to minimize**  
The sum of squared errors \((OBJ)\).

**Subject to**  
Constraints on the conversion and linear bounds on all optimization variables

Mathematically, the problem is stated as:

\[
\begin{align*}
\min \quad & OBJ \\
n_i, k_j & (i=1-3, j=Co, O, Al, O) \\
\text{s.t.} \quad & f(x, x(z), u(z), v) = 0 \\
& (C_L \leq C \leq C_U) \\
& (n_i \leq n_j \leq n_U) \\
& (k_i \leq k_j \leq k_U)
\end{align*}
\]
Table 2: Model prediction with parameters from the literature and experimental data (DBT, Co$_3$O$_4$/γ-Al$_2$O$_3$)

<table>
<thead>
<tr>
<th>LC (ppm)</th>
<th>LHSV (hr$^{-1}$)</th>
<th>Temperature (K)</th>
<th>Predicted</th>
<th>Experimental</th>
<th>Error%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1</td>
<td>403</td>
<td>822.177</td>
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<td>414.483</td>
<td>289.723</td>
<td>43.062</td>
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</tbody>
</table>

Where, $f(z, x(z), \dot{x}(z), u(z), v) = 0$ refers to the mathematical model of the process, $z$ denotes the independent variable, $u(z)$ is the optimization variable, $x(z)$ is the set of all differential and algebraic variables, $\dot{x}(z)$ represents the derivatives of differential variables with respect to $z$, and $v$ refers the fixed parameters. $C$ is the concentration and $C_L, C_U$ are the lower and upper bounds of concentration. $L$ and $U$ denote the bounds of the parameters concerned.
The optimization solution method utilized by gPROMS is a two-step way known as feasible path approach described in detail in Nawaf et al. and Jarullah et al. The values of constant factors employed in the models are listed in Table 3. Note, to avoid local minima, the solutions are checked by starting with different initial guesses of the parameters. In gPROMS, one can also provide default (initial) values of the parameters with wide bounds (lower and upper bounds).

### Table 3: Values of constant factors utilized in the ODS models

<table>
<thead>
<tr>
<th>Factors</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Initial concentration</td>
<td>C1, C2, C3</td>
<td>wt</td>
<td>C1=0.1, C2= 0.08, C3= 0.05</td>
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<tr>
<td>Temp.</td>
<td>T1, T2, T3,</td>
<td>K</td>
<td>T1= 403, T2= 443, T3= 473</td>
</tr>
<tr>
<td>Liquid hourly space velocity</td>
<td>LHSV1, LHSV2, LHSV3</td>
<td>hr⁻¹</td>
<td>LHSV1=1, LHSV2= 2, LHSV3= 3</td>
</tr>
<tr>
<td>Press.</td>
<td>P</td>
<td>Psia</td>
<td>14.7</td>
</tr>
<tr>
<td>Density of LGO at 15.6 °C and 101.3 kPa</td>
<td>Den₀</td>
<td>lb/ft³</td>
<td>52.58307119</td>
</tr>
<tr>
<td>Gas constant</td>
<td>R</td>
<td>J/mole. K</td>
<td>8.314</td>
</tr>
<tr>
<td>Volume of catalyst particle</td>
<td>Vₗ</td>
<td>cm³</td>
<td>0.00214</td>
</tr>
<tr>
<td>Total geometric external area of particle</td>
<td>Sₚ</td>
<td>cm²</td>
<td>0.0804</td>
</tr>
<tr>
<td>Bulk density</td>
<td>ρ_BCO</td>
<td>g/cm³</td>
<td>0.692</td>
</tr>
<tr>
<td>pore volume per unit mass of catalyst</td>
<td>V₉</td>
<td>cm³/g</td>
<td>0.5021</td>
</tr>
<tr>
<td>M.w of O₂</td>
<td>MWₗ</td>
<td>g/mole</td>
<td>0.21</td>
</tr>
<tr>
<td>M.w of LGO</td>
<td>MWₗ</td>
<td>g/mole</td>
<td>212.12</td>
</tr>
<tr>
<td>Critical specific volume of the DBT compound</td>
<td>V_CDBT</td>
<td>ft³/mole</td>
<td>8.2176</td>
</tr>
<tr>
<td>Mean average boiling point</td>
<td>T_meABP</td>
<td>R</td>
<td>981.27</td>
</tr>
<tr>
<td>Specific surface area of particle</td>
<td>S₉</td>
<td>cm²/g</td>
<td>2500000</td>
</tr>
<tr>
<td>Tube diameter</td>
<td>dₜ</td>
<td>cm</td>
<td>1.6</td>
</tr>
<tr>
<td>Velocity of light gas oil</td>
<td>u₁, u₂, u₃</td>
<td>cm/sec</td>
<td>u₁=0.00799, u₂= 0.01599, u₃= 0.02368</td>
</tr>
<tr>
<td>Acceleration gravity</td>
<td>g</td>
<td>cm/sec²</td>
<td>981</td>
</tr>
</tbody>
</table>

5. Results and Discussions

5.1 Experimental Results

**Effect of Catalyst Loading on Process Conversion at Operating Conditions**

The influence of initial concentration, reaction temperature, LHSV and catalyst loading on the process conversion is investigated. Below 403 K, high conversion has not been observed on the processes. No apparent difference in conversion for the oxidation of model light gas oil catalyzed by temperature of 403 K and LHSV of 3hr⁻¹ was noticed. The optimal results were obtained with a temperature of 473 K, LHSV of 1 hr⁻¹ and initial concentration of 1000 ppm. The results of experimental runs are shown in Table 4.
Table 4: Experimental results obtained from process conditions

<table>
<thead>
<tr>
<th>I.C (ppm)</th>
<th>Temp. (K)</th>
<th>LHSV(hr⁻¹)</th>
<th>Outlet concentration (ppm)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
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<td>1</td>
<td>701.760</td>
<td>0.298</td>
</tr>
<tr>
<td>1000</td>
<td>403</td>
<td>2</td>
<td>760.230</td>
<td>0.240</td>
</tr>
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<td>3</td>
<td>877.190</td>
<td>0.123</td>
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<tr>
<td>1000</td>
<td>443</td>
<td>1</td>
<td>460.640</td>
<td>0.539</td>
</tr>
<tr>
<td>1000</td>
<td>443</td>
<td>2</td>
<td>614.968</td>
<td>0.385</td>
</tr>
<tr>
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<td>443</td>
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<td>722.470</td>
<td>0.278</td>
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<td>0.780</td>
</tr>
<tr>
<td>1000</td>
<td>473</td>
<td>2</td>
<td>408.000</td>
<td>0.592</td>
</tr>
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<td>501.790</td>
<td>0.498</td>
</tr>
<tr>
<td>800</td>
<td>403</td>
<td>1</td>
<td>586.809</td>
<td>0.267</td>
</tr>
<tr>
<td>800</td>
<td>403</td>
<td>2</td>
<td>634.657</td>
<td>0.207</td>
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<td>0.104</td>
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<td>1</td>
<td>199.546</td>
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</tr>
<tr>
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<td>352.270</td>
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<td>450.436</td>
<td>0.437</td>
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<td>0.241</td>
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<td>407.661</td>
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<tr>
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<td>0.082</td>
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<td>342.989</td>
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<td>0.421</td>
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</table>

The oxidation reactivity of DBT was also investigated at different temperatures (403 – 473 K, and different LHSV (1 – 3 hr⁻¹), in the presence of the (Co₃O₄/γ-Al₂O₃) catalyst. The effects of LHSV and temperature on DBT oxidation are shown in Figure 4a. At low temperature, the oxidative conversion of DBT was very low then increased gradually with increasing reaction temperature from 403 to 473 K and the rate of DBT oxidation increased to 78 % at 473 K, 1 hr⁻¹ and 1000 ppm.
The effect of LHSV on DBT removal rate is presented in Figure 4b. It can be seen, increasing LHSV has an adverse impact on DBT conversion. Figure 4b depicts the effect of liquid flow rate on DBT conversion. As clearly noted from this Figure, DBT conversions at 1000 ppm and 473 K is 75.1% obtained at LHSV=1 hr\(^{-1}\). Note, at LHSV of 2 and 3 hr\(^{-1}\), DBT conversions were 55.9 % and 43.7 % respectively. Actually, rising liquid flow rate will lead to reduce the contact time of the reactant hence decreasing the time of reaction of DBT with air. Moreover, lower LHSV give higher liquid holdup, which evidently decrease the contact of liquid and gas reactants at the catalyst active site, by incrementing film thickness.

The sulphur content has decreased with incrementing sulphur concentration and the reaction temperature. This is due to the fact that with higher sulphur conversion its oxidative ability towards formation of corresponding sulphone derivatives decreases. As shown in Figure 4c, present study agrees to the results published by Sachdeva and Pant\(^{39}\) related to the oxidation of dibenzothiophene.

The obtained kinetic factors generated by optimization process for oxidative desulfurization operation are listed in Table below. The minimization of the objective function depending upon the sum of squared errors between the experimental and estimated results compositions, has applied to obtain the best set of kinetic factors. Optimal model parameters obtained by optimization process show in Table 5:

\[
\begin{array}{c|c|c}
\text{Parameter} & \text{Value} & \text{Units} \\
\hline
n & 1.439 & (-) \\
K1 & 0.499 & (hr^{-1} *(Wt)^{-0.43893}) \\
K2 & 1.036 & (hr^{-1} *(Wt)^{-0.43893}) \\
K3 & 2.483 & (hr^{-1} *(Wt)^{-0.43893}) \\
\end{array}
\]

Note that in our previous study (Nawaf et al.\(^{38}\)), an optimal design of TBR via improving kinetic model depending on the pilot plant experiments using different catalyst (in-house designed manganese oxide (MnO\(_2\)/γ-Al\(_2\)O\(_3\) catalyst) for the ODS of dibenzothiophene in LGO was discussed in details. It has been observed that the kinetic factors generated here are different compared with those factors obtained in our previous work, which gives a clear indication that the kinetic model for ODS process depends namely upon the kind of the catalyst utilized. The difference between the catalysts used is attributed to their differences in physical and/or chemical properties. Regarding the results of using MnOx/Al\(_2\)O\(_3\) and CoOx/Al\(_2\)O\(_3\), it seems that the activity of these catalysts is related to the metal dispersion, BET surface area, porosity, and bulk density. The catalysts are ranked as follows in terms of activity in DBT oxidation. Between the two catalysts, the manganese oxide showed a good impregnation (MnO\(_2\)=13%), compared to cobalt oxide (2%CO\(_3\)O\(_4\)).
5.2 Model Validation

The process model developed in this work is simulated further within gPROMS software. The experimental results versus simulation results obtained by the optimization technique are presented in Table 6. A comparison between experimental results and model predictions for ODS of LGO have also shown in Figures 5a, b, c, d, e which demonstrate that the model can simulate the behavior of the TBR very well within the range of operating conditions with average absolute error less than 5% among all the results obtained.

Table 6: Model prediction and experimental results (Dibenzothiophene, CoO3γ-Al2O3)

<table>
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<tr>
<th>I.C (ppm)</th>
<th>LHSV (hr⁻¹)</th>
<th>Temperature (K)</th>
<th>Concentration by Simulation</th>
<th>Conversion by Simulation</th>
<th>Experimental Concentration</th>
<th>Experimental Conversion</th>
<th>Error %</th>
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<td>500</td>
<td>3</td>
<td>473</td>
<td>295.719</td>
<td>0.409</td>
<td>289.723</td>
<td>0.421</td>
<td>2.027</td>
</tr>
</tbody>
</table>
5.3 Kinetic Analysis of Oxidation Process

The oxidation reaction of the DBT present in LGO using trickle bed reactor tested under various LHSV (1 - 3hr⁻¹), temperature (403 - 473K), initial DBT concentration (500 –1000 ppm), and catalyst (Co₃O₄/γ-Al₂O₃) in order to estimate the reaction kinetics by analyzing the results obtained based on experiments and using kinetic models within gPROMS program. The increase in process conversion happened due to the kinetic factors utilized for describing ODS processes in this model that are affected by the operating conditions. The reaction temperature affects the reaction constants of the ODS operations, where decreasing temperature leads to decrease in the reaction constants according to the Arrhenius equations (and vice versa) so that decreasing temperature decreases the number of molecules involved in the oxidation reaction, which in turn decrease the conversion (and vice versa).

LHSV is also an important operational parameters that estimates the severity of reaction and the efficiency of ODS. With the LHSV decreasing, the reaction rates will be significant. Increasing LHSV described by liquid velocity, means decreasing contact time and decreasing conversion of dibenzothiophene.

5.3.1 Activation Energy

Depending on Arrhenius correlation, a plot of (lnK) against (1/T) will give a straight line with slope equal to (-Eₐ/R), the activation energy is then evaluated as shown in Figure 6. The generated value of activation energy is introduced to be (35.425 kJ/mole). This value is close to the value obtained by Sachdeva and Pant. The low amount of $E_A$ estimated in this work pointed that the oxidation of sulphur is faster in the existence of catalyst. The reaction rate and mathematical kinetic model of dibenzothiophene that can be used with high confidence to reactor design is written as:

- Reaction rate:

$$-r_{DBT} = 18256 * EXP \left( -\frac{4260}{T} \right) * \eta_0 * \eta_{ce} * C_{DBT}^{1.43993} \quad (42)$$

Kinetic models:

$$\frac{X_{DBT}}{1-X_{DBT}} = \frac{18256*EXP\left(-\frac{4260}{T}\right)*\eta_0*\eta_{ce}*1.43993*C_{DBT}^{0.43993}}{LHSV} \quad (43)$$

Also, there are many factors affect the activation energy that can be summarized as follows:

- Firstly, one of the most important factors is the type of the catalyst. The activation energy of DBT found in the current work is in agreement with that found in the literature, which is 28.48kJ/mole using H₂O₂ and a quaternary ammonium based phosphotungstic acid as the phase transfer catalyst. However, Ahmed et
al.\textsuperscript{41} reported that the activation energy of DBT is 40.3 kJ/mole using vanadium substituted quaternary ammonium based phosphomolyb-date/H\textsubscript{2}O\textsubscript{2}/ionic liquid oxidation system.

- The second factor affecting the activation energy is the solvent type used. Ishihara et al.\textsuperscript{42} found that the activation energy of DBT and 4,6 DMDBT in two different types solvent in light gas oil equal to 32 ± 1 kJ and 28 ± 1 kJ in kerosene.

- The third factor is the type of the sulphur compound, which is individual. Such that activation energies for sulfur removal was evaluated to be 65.3 kJ/mole for DBT and 61.9 kJ/mole for BT, respectively.\textsuperscript{43} The $E_A$ of ODS for (DBT, 4-MDBT) and (4,6-DMDBT) was reported to be almost the same with a mean value of (29.1 kJ/mole) and for BT equal to 34.6 kJ/mol. The variation between the $E_A$ of BT and that of DBTs can be attributed to the electron density values on sulphur atom for BT, which is remarkably lower than that of DBTs.\textsuperscript{5}

### 5.4 Effectiveness Factor

The influence of Thiele modulus, and Effectiveness Factor on catalyst activity, are illustrated in Figures 7a, b, c. Thiele modulus and effectiveness factor is calculated according to the mathematical modeling introduced in this study within gPROMS. The following observations are made: decreasing of DBT concentration decreases Thiele modulus values slightly because it affects the values of the reaction constant as stated in Figure 7a. Therefore, the decrease of DBT concentrations increase the effectiveness factor as illustrated in Figure7b.

It is noticed from Figure 7b that the Thiele modulus and Effectiveness factor have explained why Co\textsubscript{3}O\textsubscript{4}/γ-Al\textsubscript{2}O\textsubscript{3} is the best catalyst due to the low values of Thiele modulus and high values of Effectiveness factor.

It has been noted that the effectiveness factor increases with decreasing reaction temperature and LHSV. When temperature is decreased, a more stronger decrease in the reaction constant is obtained than diffusivity. This will lead to a more pronounced diffusion limitation since it becomes the limiting step and thus to smaller effectiveness factors. When LHSV is decreased at fixed temperature, the increase in the effectiveness factor can be reported to the decreased reaction mixture viscosity, which is got at lower LHSV, since viscosity is directly related with reactants diffusivity and a decrease in viscosity will lead to an increase in effectiveness factor.\textsuperscript{44} These results agree with Figures 7b and 7c obtained from present study.
5.5 The Influence of Oxidation Process on Physical Properties of Light Gas Oil

The physical properties and ASTM distillation of feedstock and product at optimum operating condition (temperature =473K, \(LHSV=1\text{hr}^{-1}\), dibenzothiophene initial concentration =1000 ppm ) are illustrated in Table 7 and Table 8. It is obvious that there is no high difference in physical properties and ASTM distillation between feedstock and product at the optimum operating condition. This attributes to the following reasons:

- Density, viscosity, and boiling range are approximately the same before and after oxidation reaction because there was no high change in the components of hydro treated light gas oil.
- Reid vapor pressure (RVP) decrease slightly because some of volatile compounds are reacted.
- Aniline points (AN) and research octane number (RON) are the same before and after oxidation reaction approximately, due to the aromatic compounds not involved in the oxidation reaction, so that they are not break or saturated as in hydrodesulphurization process.

**Table 7**: Some physical properties of feedstock (*light gas oil*) before oxidation and after oxidation at \((LHSV=1\text{hr}^{-1}, T=473K \text{ and I.C}=1000 \text{ ppm}).

<table>
<thead>
<tr>
<th>Specification</th>
<th>LGO Before ODS</th>
<th>LGO after ODS at optimum condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVP psig (312 K)</td>
<td>16.3</td>
<td>15.8</td>
</tr>
<tr>
<td>Viscosity cst (293 K)</td>
<td>4.9</td>
<td>4.7</td>
</tr>
<tr>
<td>Density (gm/cm(^3))</td>
<td>0.8423</td>
<td>0.851</td>
</tr>
<tr>
<td>°API</td>
<td>36.4</td>
<td>34.8</td>
</tr>
<tr>
<td>Boiling range (K)</td>
<td>333-485</td>
<td>322-545</td>
</tr>
<tr>
<td>AP (K)</td>
<td>412</td>
<td>416</td>
</tr>
<tr>
<td>RON</td>
<td>87</td>
<td>83</td>
</tr>
</tbody>
</table>

**Table 8**: ASTM distillation of feedstock (*light gas oil*) before oxidation and after oxidation at \((LHSV=1\text{hr}^{-1}, T=473K \text{ and I.C}=1000 \text{ ppm}).

<table>
<thead>
<tr>
<th>Distillate volume</th>
<th>Light gas oil before ODS (K)</th>
<th>Light gas oil after ODS at optimum condition (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>433</td>
<td>447</td>
</tr>
<tr>
<td>10 %</td>
<td>481</td>
<td>487</td>
</tr>
<tr>
<td>20 %</td>
<td>499</td>
<td>504</td>
</tr>
<tr>
<td>30 %</td>
<td>514</td>
<td>523</td>
</tr>
<tr>
<td>40 %</td>
<td>531</td>
<td>538</td>
</tr>
<tr>
<td>50 %</td>
<td>545</td>
<td>557</td>
</tr>
<tr>
<td>60 %</td>
<td>563</td>
<td>569</td>
</tr>
<tr>
<td>70 %</td>
<td>581</td>
<td>587</td>
</tr>
<tr>
<td>80 %</td>
<td>599</td>
<td>604</td>
</tr>
<tr>
<td>90 %</td>
<td>624</td>
<td>630</td>
</tr>
<tr>
<td>Final</td>
<td>633</td>
<td>643</td>
</tr>
<tr>
<td>Distillate %</td>
<td>97.5%</td>
<td>98%</td>
</tr>
<tr>
<td>Loss</td>
<td>2.5%</td>
<td>2%</td>
</tr>
</tbody>
</table>
6. Conclusions

1. A model sulphur compound has investigated here to estimate the effectiveness of oxidative desulfurization operation as well as test the kinetics model of the oxidation reaction based on experiments. Generally, the oxidation of organic sulphur components under oxidative desulfurization conditions follow (1.439) order kinetic for Co3O4/γ-Al2O3 catalyst. The optimal apparent rates constant of dibenzothiophene in LGO are found to be 2.48282 (hr⁻¹ * (Wt)⁻⁰.⁴⁳⁸⁹³) at 473K for DBT. This information is very significant to design a continuous oxidative desulfurization system and the process estimation of oxidative desulfurization for LGO.

2. Optimization problem has formulated for optimizing the design and operation condition base on minimizing an objective function involving design and operating parameters.

3. Oxidation reaction simulated based on the kinetic parameters estimated from previous works gives large error percent between predicted and experimental compositions of fractions. Therefore, the optimization technique has been applied to obtain the best kinetic model depending on the experimental. The results of application of optimal kinetic parameters in simulation gives good agreement between predicted and experimental compositions with absolute less than 5% among all result and the model can now be confidently used to reactor design, operating and control, and also for predicting the concentration profiles of any component at any conditions.
Nomenclature

\( \Delta \rho_p \) Pressure dependence of liquid density \( \text{lb/ft}^3 \)

\( \Delta \rho_T \) Temperature correction of liquid density \( \text{lb/ft}^3 \)

\( C_{\text{DBT}} \) Concentration of dibenzothiophene \( \text{cm}^3/\text{mole} \)

\( C_{\text{in}} \) Initial concentration (inlet to reactor) \( \text{cm}^3/\text{mole} \)

\( C_{\text{out}} \) Final concentration (outlet from reactor) \( \text{cm}^3/\text{mole} \)

\( D_{\text{Ki}} \) Knudsen diffusivity factor \( \text{cm}^2/\text{sec} \)

\( D_{\text{ei}} \) Effective diffusivity \( \text{cm}^2/\text{sec} \)

\( D_{\text{mi}} \) Molecular diffusivity \( \text{cm}^2/\text{sec} \)

\( d_p \) Particle diameter \( \text{cm} \)

\( d_{pe} \) Equivalent particle diameter \( \text{cm} \)

\( d_t \) Tube diameter \( \text{cm} \)

\( K_a \) Frequency or pre-exponential factor \( \text{cm}^3/\text{g. sec} \)

\( K_{\text{app}} \) Apparent reaction rate constant \( - \)

\( K_{\text{in}} \) Kinetic rate constant \( (\text{time})^{-1}(\text{con.})^{1-a} \)

\( \text{MW}_i \) Molecular weight of oxygen \( \text{g}/\text{mole} \)

\( \text{MW}_L \) Molecular weight of liquid phase \( \text{g}/\text{mole} \)

\( r_{\text{DBT}} \) Dibenzothiophene rate of reaction

\( r_g \) Mean pore radius \( \text{cm} \)

\( r_p \) Radius of particle \( \text{cm} \)

\( S_g \) Specific surface area of particle \( \text{cm}^2/\text{g} \)

\( S_P \) External surface area of catalyst particle \( \text{cm}^2 \)

\( \text{Sp.gr}_{15.6} \) Specific gravity of oil at 15.6 °C \( - \)

\( T_{\text{meABP}} \) Mean average boiling point \( \text{R} \)

\( u_L \) Velocity of the liquid \( \text{cm/sec} \)

\( V_{\text{DBT}} \) Critical specific volume of the DBT compound \( \text{ft}^3/\text{mole} \)

\( V_{\text{CL}} \) Critical specific volume of liquid \( \text{cm}^3/\text{mole} \)

\( V_{\text{DBT}} \) Molar volume of DBT at n.b. temperature \( \text{cm}^3/\text{mole} \)
$V_g$  Total pore volume  \( \text{cm}^3/\text{g} \)

$V_L$  Molar volume of liquid at its n.b. temperature  \( \text{cm}^3/\text{mole} \)

$V_P$  Volume of catalyst particle  \( \text{cm}^3 \)

$\mu_L$  Dynamic viscosity of liquid phase  \( \text{mPas. sec} \)

$\rho_{15.6}$  Density of light gas oil at 15.6 °C  \( \text{g/cm}^3 \)

$\rho_B$  Bulk density  \( \text{g/cm}^3 \)

$\rho_L$  Liquid density at process condition  \( \text{lb/ft}^3 \)

$\rho_o$  Density of light gas oil at 15.6 °C and 101.3 Kpa  \( \text{lb/ft}^3 \)

$\rho_p$  Particle density  \( \text{g/cm}^3 \)

A  Dimensionless number  -

EA  Activation energy  \( \text{kJ/mole} \)

$F_{\text{DBT}}$  Input of dibenzothiophene  moles/time

$g$  Acceleration  \( \text{cm/sec}^2 \)

K  Reaction rate constant  \( \text{hr}^{-1}.\text{wt}^{(n-1)} \)

n  Order of reaction kinetic  -

ppm  Part per million  -

R  Universal gas constant  \( 8.314 \text{ J/mol. K} \)

T  Temperature  K or °C

V  Bed volume of particle catalyst  \( \text{cm}^3 \)

$V_L$  Volumetric flow of liquid phase  \( \text{cm}^3/\text{time} \)

$V_P$  Pore volume  \( \text{cm}^3 \)

$\tau$  Residence time  hr

**Greek letters**

$\eta_{ce}$  External catalyst wetting efficiency

$\epsilon_S$  Catalyst porosity

$\tau$  Tortuosity factor

$\Phi$  Thiele modulus

$\epsilon_B$  Bed void fraction
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Alumina pre-treatment
\( (\gamma\text{-Al}_2\text{O}_3) \)

Preparation of noble metal solution
(Cobalt solution)

Incipient Wetness Impregnation
(IWI)

Drying

Calcination

Figure 1
Figure 2
Light gas oil

Operation Model:
1. Co-current
2. Isothermal

Processing and Reactor Type:
1. Steady state
2. Trickle bed
3. Continuous

Catalyst Bed
30%

Kinetic Data: ODS
1. Parameters
2. Models of reaction

Required Data:
Physiochemical properties:
1. Diesel viscosity
2. Diesel density
3. Diffusivities
4. etc

Tools Variable:
1. Mass balance equations:
2. Numerical tool (gPROMS general process modeling system)

Light Gas Oil Desulphurization

Operation Variable:
1. Temperature (T)
2. Liquid hourly space velocity (LHSV)
3. Initial concentration of (DBT)

Figure 3
Figure 4
Figure 5
Figure 6

\[ y = -4260.9x + 9.8123 \]

\[ R^2 = 0.9745 \]
Figure 7