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# Kinetic parameter estimation and simulation of trickle-bed reactor for hydrodesulfurization of crude oil

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ABSTRACT

Hydrodesulfurization (HDS) of crude oil has not been reported widely in the literature and it is one of the most challenging tasks in the petroleum refining industry. In order to obtain useful models for HDS process that can be confidently applied to reactor design, operation and control, the accurate estimation of kinetic parameters of the relevant reaction scheme are required. In this work, an optimization technique is used in order to obtain the best values of kinetic parameters in trickle-bed reactor (TBR) process used for hydrodesulfurization (HDS) of crude oil based on pilot plant experiment. The optimization technique is based on minimization of the sum of the square errors (SSE) between the experimental and predicted concentrations of sulfur compound in the products using two approaches (linear (LN) and non-linear (NLN) regressions).

A set of experiments were carried out in a continuous flow isothermal trickle-bed reactor using crude oil as a feedstock and the commercial cobalt–molybdenum on alumina (Co–Mo/$\gamma$-$Al_2O_3$) as a catalyst. The reactor temperature was varied from 335 to 400 °C, the hydrogen pressure from 4 to 10 MPa and the liquid hourly space velocity (LHSV) from 0.5 to 1.5 $h^{-1}$, keeping constant hydrogen to oil ratio ($H_2$/oil) at 250 L/L.

A steady-state heterogeneous model is developed based on two-film theory, which includes mass transfer phenomena in addition to many correlations for estimating physiochemical properties of the compounds. The hydrodesulfurization reaction is described by Langmuir–Hinshelwood kinetics. gPROMS software is employed for modelling, parameter estimation and simulation of hydrodesulfurization of crude oil in this work. The model simulations results were found to agree well with the experiments carried out in a wide range of the studied operating conditions. Following the parameter estimation, the model is used to predict the concentration profiles of hydrogen, hydrogen sulfide and sulfur along the catalyst bed length in gas, liquid and solid phase, which provides further insight of the process.



## 1. Introduction

Crude oil is a very complex material consisting of different hydrocarbon compounds in addition to sulfur, nitrogen, oxygen and some metallic compounds, containing nickel, vanadium, iron and copper (Ali and Abdul-Karim, 1986). Market demands for different crude oil derivatives are high. The average consumption of different fuels such as Gasoline, Kerosene, Jet fuels is 40–50% of crude oil consumption and worldwide consumption may exceed 70% in the next years (Ray et al., 1995). Therefore, it was necessary to increase distillate production at high quality.

The presence of sulfur, nitrogen, oxygen and metallic compounds in crude oil has a significant impact upon the quality of oil products in addition to the harm they can cause. Sulfur compounds lead to environmental pollution through atmospheric contamination by oxidization resulting from combustion forming sulfur dioxides, which will be oxidized later with ultraviolet rays to $SO_3$. These compounds react with atmospheric water to form sulfuric acid that causes many lung diseases, like asthma and shortness of breath. It also leads to soil pollution with acid materials, decreases the life of machinery, corrodes of pipes, machines and equipment, affecting the additives used for the purpose of increasing the octane number, reduce the activity of Tetra Ethyl Lead (TEL) added to gasoline. In addition, these impurities cause catalyst poisoning and reduce the catalyst activity. Therefore, the environmental regulations have enforced substantial decrease of sulfur compounds in fuels (Gajardo et al., 1982; Kim and Choi, 1987; Mahmood et al., 1990; Andari et al., 1996; Speight, 2000).

The hydrotreating process is one of the most important processes in the refineries to reduce the content of the sulfur, nitrogen, oxygen and metallic compounds from oil fractions at high

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temperatures and hydrogen pressures. All the hydrotreating processes are conducted on the oil fractions (i.e. after the separation of crude oil to its derivatives such as gasoline, kerosene, heavy and light gas oil and other oil fraction), and not on the full crude oil. This means that a large part of the contaminants, such as sulfur, nitrogen, metals, aromatics and asphaltenes will be deposited at the bottom of the atmospheric and vacuum distillation column. Hydrotreating process of each section separately is fairly easy. However, the crude oil hydrotreating process is regarded as a large and difficult challenge since crude oil contains many compounds and complex structures, in addition to multiple phases. As well as, crude oil hydrotreating in the presence of the asphaltenes containing a large component of sulfur and metals (which close the active sites of the catalyst) is one of the more difficult and important problems.

The development of a mathematical model of the hydrotreating process of crude oil is a hard task in view of the intricate chemical and physical changes that are undergone in the feed together with transport phenomena and mechanisms of catalyst deactivation in the reaction system, the main challenge being the estimation of the kinetic parameters accurately. It is necessary to develop kinetic models that can accurately predict the product compounds under various process conditions. For hydrodesulfurization reactions, the development of such kinetic models is a challenging task due to the presence of a great variety of structures. The main focus in this paper is therefore to determine these parameters based on experimental data. The experiments were conducted in a continuous flow, isothermal trickle-bed hydrotreating pilot plant reactor. The basic model is taken from the literature and the kinetic parameters are obtained by minimizing sum of the squared error between experimental data and model prediction. Finally, the model is used for simulation of the hydrodesulfurization (HDS) process carried out using the general PROcess Modelling System (gPROMS) software (gPROMS, 2005).

## 2. Mathematical model of TBR

Building models is one of the major occupations of engineering and science. Models are used because it is too expensive or time consuming or risky to use real system to evaluate plant performance. Models are typically employed in engineering design and optimization because they offer the cheapest and faster way of studying the impacts of changes in design variables on system performance. An essential stage in the improvement of any model is the formation of the appropriate mass and energy balance equations. To these should be added suitable kinetic equations of chemical reaction rates, rates of mass and heat transfer and equations representing process property variations. The basic mathematical model can be provided by combination of these relationships (Ingham et al., 1994).

In this study, a three-phase heterogeneous reactor model is developed and applied to obtain kinetic parameters for crude oil HDS reaction and to analyse the performance of a pilot plant TBR. The reactor model includes a set of differential equations and algebraic equations. The model comprises of correlations for estimating gas–liquid and liquid–solid mass transfer coefficients, solubility data, and properties of the compounds, such as densities, viscosities, diffusivities and molar volume at process conditions using information presented in the literature (Froment et al., 1994; Jimenez et al., 2005; Alvarez and Ancheyta, 2008). The reactor temperature along the catalyst bed length is assumed to be constant, and thus, the differential equation concerning heat balance is neglected.

The three phases in the reactor are: fixed bed of catalyst particles (solid phase), hydrogen (gas phase) and oil feedstock (liquid phase). Trickle-bed reactor process is marked by the simultaneous existence of gas and liquid, over and through a third catalyst solid phase in a cocurrent flow mode (Bhaskar et al., 2002; Avraam and Vasalos, 2003; Shokri et al., 2007), which is considered in this work.

The following assumptions were used to create the mathematical model:

(a) There are no radial concentration gradients.
(b) The reactor is operated at steady state.
(c) One-dimensional heterogeneous model.
(d) The reactor operates isothermally.
(e) The phase change of light cuts is negligible.

Note, these assumptions are valid and adequate to represent the pilot plant study presented in this work. The reactor size (2 cm in diameter and 65 cm in length) is small and therefore one-dimensional model is justified. Isothermal condition is mentioned in the pilot plant throughout the experiment (see Section 4.3). Also, note that experimental data were collected at steady-state condition of the reactor. The pilot plant system is closed and the reactor pressure is very high (10 MPa). Therefore, negligible phase change of light cuts is justified.

The required data and the available tools with the assumptions for modelling and simulation of crude oil hydrodesulfurization are highlighted in Fig. 1.

### 2.1. Mass balance equations in gas phase

$$\text{Hydrogen}: \quad \frac{dP^G_{H_2}}{dz} = -\frac{RT}{u_g} k^L_{H_2} a_L \left( \frac{P^G_{H_2}}{h_{H_2}} - C^L_{H_2} \right) \tag{1}$$

$$H_2S: \quad \frac{dP^G_{H_2S}}{dz} = -\frac{RT}{u_g} k^L_{H_2S} a_L \left( \frac{P^G_{H_2S}}{h_{H_2S}} - C^L_{H_2S} \right) \tag{2}$$

Eqs. (1) and (2) include a system of ordinary differential equations (ODEs) that relate the partial pressures of $H_2$ and $H_2S$ to the mass transfer of the compounds across the gas–liquid interface. These equations can be solved to give partial pressure profiles of hydrogen and hydrogen sulfide along the catalyst bed length when the concentrations of these compounds in the liquid phase are known.

### 2.2. Mass balance equations in liquid phase

The differential equations of mass balance for the concentrations of hydrogen and hydrogen sulfide in the liquid phase can be written by equating the concentrations gradient to the mass transfer of $H_2$ and $H_2S$ across the gas–liquid and liquid–solid as follows:

$$\text{Hydrogen}: \quad \frac{dC^L_{H_2}}{dz} = \frac{1}{u_l} \left[ k^L_{H_2} a_L \left( \frac{P^G_{H_2}}{h_{H_2}} - C^L_{H_2} \right) - k^S_{H_2} a_S \left( C^L_{H_2} - C^S_{H_2} \right) \right] \tag{3}$$

$$H_2S: \quad \frac{dC^L_{H_2S}}{dz} = \frac{1}{u_l} \left[ k^L_{H_2S} a_L \left( \frac{P^G_{H_2S}}{h_{H_2}S} - C^L_{H_2S} \right) - k^S_{H_2S} a_S \left( C^L_{H_2S} - C^S_{H_2S} \right) \right] \tag{4}$$

Eqs. (3) and (4) represent the mass balance equations for the gaseous compounds ($H_2$ and $H_2S$), while the mass balance equation for the liquid compounds (sulfur) can be written by equating their liquid-phase concentration gradients to their mass transfer between the liquid phase and the solid phase. For the sulfur compound in liquid phase, the mass balance equation can be