



Ultra low sulfur diesel simulation. Application to commercial units

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HIGHLIGHTS

- ▶ An ULSD simulation on pilot plant and industrial hydrodesulfurization process was applied.
- ▶ Experimental data from pilot plant using different gasoils and commercial catalysts was generated.
- ▶ Commercial catalysts with similar activity were tested at close operating conditions.

ARTICLE INFO

Article history:

Received 29 March 2012
 Received in revised form 27 September 2012
 Accepted 29 September 2012
 Available online 3 December 2012

Keywords:

Hydrodesulfurization
 Ultra low sulfur diesel
 Kinetic model

ABSTRACT

A kinetic model for the hydrodesulfurization process to obtain ultra low sulfur diesel (ULSD) was applied to commercial units proving its capabilities. The model was developed from the experimental data that were generated in a pilot plant with three commercial catalysts (A, B and C), using straight run gasoil (SGO), light cycle oil (LCO), light cracked gasoil (LCGO) and their blends as feedstocks. The model was compared with operational data of one refinery of Latin America. Typical conditions have been covered by the simulation analysis (340–370 °C, 0.7–1.5 h⁻¹, and 60–80 kg/cm², for temperature, space velocity and pressure, respectively) in order to obtain model predictions compared to those used in practical industrial applications.

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1. Introduction

An essential problem for refiners is the production of ULSD, so an understanding of the principles that govern the ULSD operation is mandatory. Fundamental models are useful for design, operation, and control of hydrodesulfurization (HDS) units. Also, reliable sulfur reaction mechanisms can provide best solutions to achieve the required ULSD specifications.

In the last years, legislations around the world have been promoted ULSD production to improve the quality of fuels, as well as to minimize the air pollution caused by combustion. Environmental regulations have been introduced in many countries to reduce the sulfur content of diesel fuel to ultra low levels (10–15 ppmw).

The hydro-treating (HDT) process has suffered few changes along the time; the core part is, as always, the reactor and the specific catalysts that are used to obtain a desired product.

Many works have been reported around the HDS process and the production of ULSD [1]. Some of these works emphasize the contribution of kinetic models for detection and correction of

operation errors, as well as the reduction of investment costs [2–6]. On the other hand, some studies focus on the evaluation of commercial catalysts [7,8], whereas other studies have been proving their attention on the mathematical modeling for HDS processes [9–17]. Also, there are studies on dynamic heterogeneous models of trickle bed reactors for gasoil hydro-treating (HDT) [18–23].

In 2006, a dynamic heterogeneous one-dimensional model of trickle-bed reactors for HDT of vacuum gas oil (VGO) using a NiMo/Al₂O₃ commercial catalyst was developed by Mederos et al. [18]. In that work, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodearomatization (HDA) reactions were considered into a dynamic model that was validated by using experimental data from isothermal pilot plant, and it was applied to predict the dynamic behavior of commercial hydro-treating reactors.

In 2007, the hydrogenation of oil fractions on trickle-bed reactors with concurrent and countercurrent operation modes was predicted by Mederos and Ancheyta [19]. Those authors founded a superior performance of countercurrent operation mode over concurrent mode.

A discussion of possible approaches for quenching a VGO hydrotreater was presented by Alvarez and Ancheyta in 2008 [20]. Here the behavior of different process schemes using a HDT reactor

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Nomenclature

C_i	molar concentration of component i (mol/cm ³)	K_{i-}	backward reaction rate constant (mol/g s)
BPH	biphenyl	LC	level control
CHB	cyclohexylbenzene	LCGO	light cracked gasoil
DBT	dibenzothiophene	LCO	light cycle oil
F_i^0	molar flow at the reactor inlet (mol/s)	$LHSV$	liquid hourly space velocity (h ⁻¹)
F_i	molar flow at the reactor outlet (mol/s)	P	partial pressure (kg/cm ²)
H ₂	hydrogen	PC	pressure control
H ₂ S	hydrogen sulfide	PI	pressure indicator
HC	hydrocarbon	PIC	pressure indicator control
HDA	hydrodearomatization	r_i	rate of reaction (mol/g s)
HDN	hydrodenitrogenation	SGO	straight run gasoil
HDS	hydrodesulfurization	TC	temperature control
HDT	hydro-treating	ULSD	ultra low sulfur diesel
k_i	adsorption equilibrium constant (mol/cm ³)	VGO	vacuum gasoil
K_i	forward reaction rate constant (mol/g s)	w	weight factor
$K_{i,\sigma}$	adsorption equilibrium constant of component i on σ -sites (cm ³ /mol)	33dmBPH	3,3-dimethylbiphenyl
$k_{i,\sigma}$	rate coefficient for the hydrogenolysis of component i (mol/g s)	46dmDBT	4,6-dimethyldibenzothiophene
$K_{i,\tau}$	adsorption equilibrium constant of component i on τ -sites (cm ³ /mol)	<i>Greek symbols</i>	
$k_{i,\tau}$	rate coefficient for the hydrogenation of component i (mol/g s)	σ	hydrogenolysis site
		τ	hydrogenation site

model with an inter-bed quenching was proposed. The effect of quench fluid on the overall performance of the reactor was presented, and generalized HDS, HDN and HDA reactions were assumed.

Based on literature review, three factors (plug flow deviation, external wetting efficiency and wall effect) involved on trickle-bed reactor performance was discussed by Fabian et al. in 2009 [21]. After their analysis, the authors conclude that non-uniformities in the external liquid wetting of catalyst pellets affect much more the reactor behavior than deviation from plug flow, wall flow or the liquid–solid mass transfer resistance. Also, the intra-particle and inter-phase gradients were not considered as limiting factors of kinetic, because the mass transfer coefficients in trickle bed reactors for hydro-processing are usually high and not limiting.

Different alternatives for modeling HDT process were presented by Mederos et al. in 2009 [22], who were focused on detailed deterministic reactor model. Using the modeling aspects widely published and discussed in literature, a generalized reactor model was developed by those authors, who provide some guides for the estimation of model parameters. Those authors have postulated that reliable modeling and simulation of deep removing of impurities in HDT process is possible by studying the typical characteristics of feeds, where identification of compounds with similar reactivity is the most important step.

Recently, in 2012 [23], a dynamic heterogeneous one-dimensional model of trickle-bed reactor used for catalytic hydro-treating of oil petroleum fractions was developed by Fabian et al. The model developed by those authors takes into account the HDS, HDN, HDA, hydrogenation of olefins and mild hydrocracking reactions. Kinetic parameters were determined from experimental data obtained in a bench scale isothermal reactor during the hydro-treating process of atmospheric gasoil coming from heavy oil on a commercial CoMo catalyst.

In this work, the hydrodesulfurization simulation by kinetic model of trickle-bed reactors is presented. The results were validated with data generated in a pilot plant. Also, three commercial catalysts (A, B and C) and different gasoils (SGO, LCO and LCGO) at typical operating conditions were tested.

2. Experimental procedure

2.1. Pilot plant configuration

Fig. 1 shows the pilot plant configuration; briefly the way at which operate is described. Hydrogen (99.8%) coming from limits of one battery is passed through the flow controller pre-heated up to about 100 °C. The liquid is weighted and pre-heated before mixing with hydrogen and introduced into the isothermal fixed bed reactor, with capacity of 150 ml. That reactor has sensors for both pressure and temperature. The reactor is loaded with commercial catalyst and operated in down-flow mode. The temperature in the reactor is controlled along the fixed bed using a thermocouple of five points that is contained in a thermo-well extended along the center of the reactor. The reactor temperature is maintained at the desired level by electric heaters which provide the isothermal temperature requirement along the active reactor section. The deviation from the desired value is 1 °C.

Once the product is obtained, it is transported to the separation unit. First, the product is passed through a high pressure and high temperature separator, which operates at the same conditions than the reactor. The gas phase obtained in the top of the separator is transported to a second high pressure and low temperature (25 °C) separator, where the liquid drops are dragged and recovered. Then, the gas is passed through the valve where the pressure is decreased down to 2 kg/cm² and introduced in a gas-meter where it is measured and analyzed. The remaining gas is discarded to the atmosphere with a prior caustic treatment. Also, the liquid obtained from the bottom of the separators is collected, measured and analyzed. Any trace of H₂S into the liquid sample is removed via nitrogen stripping and washed with an aqueous solution of NaOH at 5 wt.% previous to the analysis of products.

2.2. Hydro-treating experiments

Hydro-treating experiments were carried out according to standard industrial conditions by using temperatures of 320, 340, 350, 360 and 370 °C; pressures of 60 and 80 kg/cm²; $LHSV$

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