



Dynamic modeling of an industrial diesel hydroprocessing plant by the method of continuous lumping

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ABSTRACT

Diesel hydroprocessing is an important refinery process which consists of hydrodesulfurization to remove the undesired sulfur from the oil feedstock followed by hydrocracking and fractionation to obtain diesel with desired properties. Due to the new emission standards to improve the air quality, there is an increasing demand for the production of ultra low sulfur diesel fuel. This paper is addressing the development of a reliable dynamic process model which can be used for real-time optimization and control purposes to improve the process conditions of existing plants to meet the low-sulfur demand. The overall plant model consists of a hydrodesulfurization (HDS) model for the first two reactor beds followed by a hydrocracking (HC) model for the last cracking bed. The models are dynamic, non-isothermal, pseudo-homogeneous plug flow reactor models. Reaction kinetics are modeled using the method of continuous lumping which treats the reaction medium as a continuum of species whose reactivities depend on the true boiling point of the mixture. The key modeling parameters are estimated using industrial data. Steady-state and dynamic model predictions of the reactor bed temperatures, sulfur removal, and diesel production match closely the plant data.

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1. Introduction

Diesel is a petroleum fossil fuel that contains different forms of sulfur compounds including mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophenes, and substituted dibenzothiophenes. Combustion of sulfur compounds in diesel engines emits sulfur oxides into the atmosphere, which can cause detrimental effects on the human health and the environment. In order to comply with the new emission standards to improve the air quality, there is an increasing demand for the production of ultra low sulfur diesel (ULSD) fuel (<10 ppm). In the future, this trend toward “zero” sulfur diesel is expected to continue (Stanislaus et al., 2010). In order to meet the low-sulfur demand, refineries are considering alternative revamping strategies such as design changes, new catalysts and improvements in process (Palmer et al., 2003). In parallel with increasing market demand for low sulfur diesel, research in the production of ULSD has gained increased popularity in the scientific community (Stanislaus et al., 2010).

The simplified flowsheet for the industrial diesel hydroprocessing (DHP) plant is shown in Fig. 1. The plant is designed to process 4500 cubic meters per day of diesel feedstock. The process consists of a blending section followed by three catalytic reactor beds which consist of two hydrodesulfurization (HDS) and one hydrocracking (HC) bed. The feed is obtained by blending four streams: HD (straight run heavy diesel), LD (straight run light diesel), LVGO (light vacuum gas oil) and an imported diesel. HD and LD streams are derived from a crude distillation unit, and LVGO stream is derived from another vacuum distillation unit. Imported diesel's specifications are close to the product specifications of the DHP Plant except the sulfur content. It is used as an additive in order to keep the product T95 value (the temperature at which 95% of the distillate is collected, e.g., by ASTM D86 distillation) at desired specifications. These streams are blended in order to obtain a desired T95 value for the reactor charge. The blended feed is mixed with the recycle hydrogen gas (treat gas) before it enters the furnace where it is heated to the required reactor inlet temperature. Hydrodesulfurization occurs at high temperatures in the presence of excess hydrogen to produce higher-value hydrocarbon products with lower sulfur levels. In the first two catalytic HDS beds (usually with CoMo/Al₂O₃ or NiMo/Al₂O₃ catalysts), the organic sulfur

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Nomenclature

T	bed temperature (K)
T_0	reference temperature (K)
TBP	true boiling point ($^{\circ}\text{C}$)
$TBP(h)$	highest boiling point ($^{\circ}\text{C}$)
$TBP(l)$	lowest boiling point ($^{\circ}\text{C}$)
C_p	heat capacity (kJ/kg K)
ΔT	bed temperature difference ($^{\circ}\text{C}$)
v	average velocity (m/h)
$C(t)$	concentration (kg/kg feed)
$c(k,0,0)$	initial concentration of species at the reactor inlet (kg/kg feed)
$k_{\min 1}$	minimum reactivity of sulfur species in Bed 1 (h^{-1})
$k_{\min 2}$	maximum reactivity of sulfur species in Bed 2 (h^{-1})
k	reactivity (h^{-1})
$D(k)$	species type distribution function
$k_{\max 1}$	maximum reactivity of sulfur species in Bed 1 (h^{-1})
$k_{\max 2}$	maximum reactivity of sulfur species in Bed 2 (h^{-1})
wt	weight fraction
K	maximum reactivity in the hydrocracker (h^{-1})
N	number of sulfur species
E_{a1}	activation energy in Bed 1 (kJ/kmol)
E_{a2}	activation energy in Bed 2 (kJ/kmol)
ΔH_1	heat of reaction in Bed 1 (kJ/kg sulfur)
ΔH_2	heat of reaction in Bed 2 (kJ/kg sulfur)
$k_{hc,\max}$	maximum reactivity of hydrocarbon species in the hydrocracker bed (h^{-1})
$E_{a,hc}$	activation energy for the hydrocracking reactions (kJ/kmol)
c	parameter for the heat of cracking reaction
d	parameter for the heat of cracking reaction
Greek letters	
θ	normalized boiling point
α	the parameter that relates cracking reactivity to normalized boiling point
α_0	the parameter in the yield function
α_1	the parameter in the yield function
β	the parameter that relates HDS reactivity to the normalized boiling point

compounds are converted to hydrogen sulfide. Reactors operate at high pressures (3.0–5.0 MPa) and temperatures (300–450 $^{\circ}\text{C}$). Hydrogenation reactions are exothermic; therefore, reaction products are cooled by the hydrogen quench flows between the beds. Hydrocracking (HC) occurs in the third bed in which the high-boiling, high molecular weight hydrocarbons crack to lower-boiling point species. The last (fourth) bed is used for dewaxing to improve the cold flow properties during winter operation. The presented model does not include this bed since it covers the days of summer diesel operation when the last bed was inactive. HDS and HC units are trickle bed reactors in which the liquid phase consists of the heavy gas oil feed; hydrogen is in the gas phase and the catalyst constitutes the solid phase. The HC product is separated into the end products which are the diesel and the naphtha. Important product specifications are the sulfur content and T95 value for the diesel.

The kinetics of hydrodesulfurization is complex since the diesel feedstock contains a variety of organic sulfur compounds. In general, the difficulty of sulfur removal increases in the order: paraffins < naphthenes < aromatics (Ancheyta, 2011). Reactivities of different sulfur compounds depend on their boiling points as shown in Fig. 2 (Song, 2003). For treating the oil to lower and

lower sulfur levels, it is necessary to remove sulfur from the heavier hydrocarbon fractions that are the most difficult to desulfurize. As shown in Fig. 2 (Song, 2003), the higher molecular weight dibenzothiophenes are sterically hindered refractive compounds that are the most difficult to treat.

Typical HDS reactions are shown in Fig. 3 (Gruia, 2006). Mechanistic kinetic modeling of hydrodesulfurization is a challenging task because of the large number of compounds participating in many complex reactions. In this work we use the continuous lumping method that considers the reactive mixture as a continuum (Aris and Gavalas, 1966; Chou and Ho, 1988). Continuous lumped models are relatively easy to develop, and they have fewer number of modeling parameters to estimate. At the same time they are known to possess good predictive capabilities (Elizalde and Ancheyta, 2012).

Eventually, we want to use the developed model for optimization and control of the industrial unit. For this reason, the model should be able to predict both the steady-state and the dynamic behavior of the actual process. At the same time, while capturing the essential features of the industrial process, unnecessary details which can hinder its end use must be avoided. Therefore, in this work, instead of an heterogeneous multi-dimensional model, we choose to develop a pseudo-homogeneous, one-dimensional dynamic reactor model. Similarly, instead of a more detailed mechanistic kinetic model, we use a continuous lumping based kinetic model.

2. Model

2.1. Mathematical preliminaries for continuous lumping

For a mixture that has N reactant species, the total concentration at time t is given by

$$C(t) = \sum_{i=1}^N c_i(t) \quad (1)$$

where $c_i(t)$ is the concentration of the i th reactant and $C(t)$ is the total concentration. In our case for the HDS beds, the reactant is the sulfur compound.

In Chou and Ho (1988), the above discrete mixture was approximated by a continuous mixture where the concentrations are continuous functions of reactivity k . This is achieved by a coordinate transformation from discrete “ i -coordinate” to continuous “ k -coordinate” given by:

$$D(k_i) = \frac{\Delta i}{\Delta k_i} \quad (2)$$

As the number of species N approaches infinity, $D(k_i)$ becomes a continuous function of k and $D(k)dk$ represents the number of species with reactivity between k and $k + dk$. With these definitions, one gets the continuous representation of the discrete mixture:

$$C(t) = \int_0^{\infty} c(k, t) D(k) dk \quad (3)$$

where $c(k, t)$ is the concentration of reactant with reactivity k at time t in the continuous mixture. $D(k)$ is known as the species-type distribution function.

The literature suggests that for HDS reactions, the reactivity of sulfur species decreases monotonically with the true boiling point (TBP). Accordingly, the following relationship has been used to model this dependency (Sau et al., 1997):

$$k = k_{\min} - k_{\max} \ln[e^{-1} - (e^{-1} - 1)\theta^{1/\beta}] \quad (4)$$

where k_{\min} , k_{\max} and β are adjustable (to be estimated) parameters and variable θ is the normalized true boiling point. Fig. 4 shows how

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