



Predictive modeling and optimization for an industrial Coker Complex Hydrotreating unit – development and a case study



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ABSTRACT

This work presents a model for UOP Coker Complex Hydrotreating Process using Aspen HYSYS Petroleum Refining module. The model depends on routinely taken industrial data of process streams during normal operating conditions. Acquired data sets have been tested and screened in order to ensure data validity for building the model and avoiding erroneous results. A detailed kinetic model of hydrotreating reactions in the reactor has been applied. The trickle bed reactor (TBR) model has been validated using 3 months of industrial plant data. In addition, rigorous tray-by-tray simulations for hydrogen sulfide absorption tower and TBR effluent fractionation tower have been utilized to match the performance of the plant's towers. The model has been used then for studying the effects of different process variables on the plant performance. In addition, the model has been used in optimizing the operating conditions of the process. This optimization showed a potential for notable savings of fuel and energy consumption in the process, while increasing the process productivity.

1. Introduction

In the recent decades, petroleum refiners' interests have trended toward obtaining a fuel with low environmental pollutants such as sulfur, nitrogen and aromatics instead of maximizing conversion of heavy oil to liquid fuels. World regulations have imposed legislations in order to minimize SO_x and NO_x emissions as well as soot particles from both refiners' flares and their products after burning. Therefore, recent environmental regulations take strict decisions towards refiners that contravene the allowable proportions of these pollutants in their products. For example, U.S. Environmental Protection Agency has begun enforcing deterrent rules that determine the maximum quantities of sulfur compounds in diesel fuel since mid-2006 [1].

Quality of extracted crude oils has diminished over the last two decades as a result of ongoing efforts to discover new oil fields in order to fulfill the global fuel demand. Therefore, environmental pollutants already exist in the current crudes in large quantities, adversely affecting the human and ecosystem. Hydrotreating is thought to be one of the effective solutions to generate a fuel compatible with environmental regulations. Therefore, refiners now increase hydrotreating severity in order to make their products identical to the standard specifications [2]. In general, hydrotreating is designed primarily to remove the sulfur and nitrogen. In addition, this process performs an excellent job of saturating olefinic and aromatic compounds for producing a commercial jet and diesel fuel. Liquid fuels produced from hydrotreating

reactors are highly desirable with respect to environmental regulations due to their few pollutants content and high performance inside the engines.

Trickle bed reactor (TBR) is widely used in hydrotreating. TBR is three phases, trickle flow regime, fixed bed reactor where hydrogen and hydrocarbons concurrently flow downward over a fixed bed of catalyst particles while hydrotreating reactions occur. Liquid hydrocarbons travel down as a laminar film and/or in rivulets over the solid particles, whereas hydrogen passes through the remaining void space. Dissolved hydrogen and hydrocarbons molecules diffuse through the catalyst surface in order to find the distributed active sites. Therefore, the elevated pressures are preferred inside TBRs to improve the gas solubility and molecular diffusivity during hydrotreating. Usually, TBRs operate adiabatically at high temperatures to promote hydrotreating, inasmuch as the kinetics and thermodynamics of most reactions improve when the temperatures of TBRs are raised [3–5].

Hydrotreating TBR catalysts consist of promoted MoS₂ or WS₂ particles uniformly distributed on supports with high surface area such as macro porous alumina or zeolite. Co, Ni, or both are added as promoters to bridge with Mo or W atoms in order to provide the active sites required for hydrotreating reactions. The selectivity of Co and Ni towards these reactions differs. CoMo catalysts have a higher HDS performance at low operating pressures compared to NiMo catalysts. However, CoMo catalysts have a lower HDN performance. NiCoMo catalysts combine between CoMo and NiMo catalysts benefits.

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Nomenclature

CCR	Conradon Carbon Residue
DEA	Di ethanolamine
EOB	End of Run
FBP	Final boiling point
HA	Heavy aromatic compounds
HDA	Hydrodeasphaltenization
HDM	Hydrodemetallization
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydro desulfurization
HN	Heavy naphthenic compounds
HNA	Heavy naphthenic aromatic compounds
HNi	Heavy nitrogen compounds
HP	Heavy paraffinic compounds
HS	Heavy sulfur compounds
IBP	Initial boiling point
L	Light compounds
LA	Light aromatic compounds
LN	Light naphthenic compounds

LNi	Light nitrogen compounds
LP	Light paraffinic compounds
LS	Light sulfur compounds
MA	Medium aromatic compounds
MN	Medium naphthenic compounds
MNA	Medium naphthenic aromatic
MNi	Medium nitrogen compounds
MP	Medium paraffinic compounds
MS	Medium sulfur compounds
TBR	Trickle bed reactor
VA	Vacuum aromatic compounds
VN	Vacuum naphthenic compounds
VNA	Vacuum naphthenic aromatic
VNi	Vacuum nitrogen compounds
VP	Vacuum paraffinic compounds
VS	Vacuum sulfur compounds
WABT	Weight average bed temperature
ψ	Property of a petroleum fraction
θ	Known property of a petroleum fraction
w_i	Weighting factor of process variable i
X_i	Process variable i

Industrially, more than one type of these catalysts is used inside TBR. NiMo catalysts are often put as a protective layer to the main catalyst against deactivation by olefins and gum precursors [6–11]. On the other hand, physical characteristics of TBR catalysts such as pore volume, bulk density, shape and size influence catalyst effectiveness factors and thus heat and mass transfer rates [12–14]. Catalysts with large pores are preferred for demetallization, whereas catalysts with small pores are favored for desulfurization. Therefore, catalyst characteristics beside reactions kinetics should be considered during TBR modeling.

Modeling of an industrial hydrotreating unit generally requires process identification. An industrial data is usually utilized in order to recognize the relations between the real system variables due to the nonlinearity of these relations as well as the complexity of process chemistry. However, several published researches developed a kinetic model for HDS and HDN reactions based on experimental data in order to predict the behavior of industrial catalysts inside TBRs during hydrotreating of oil fractions. Mederos and Ancheyta [15–17] developed a kinetic model considering the main reactions present in hydrotreating process in order to compare between co-current and counter-current operation modes of TBRs. They utilized the kinetic parameters obtained from experimental data to predict the dynamic behavior of industrial hydrotreating TBRs. Rodríguez et al. [18] modeled kinetics of HDS with power law approaches and Langmuir-Hinshelwood approach using the data reported by Mederos and Ancheyta [15–17] in order to compare between the results of different kinetic models. Alvarez et al. [19,20] developed a kinetic model to investigate the hydroprocessing behavior with both gas and liquid quenching in a multi-fixed-bed reactor. In addition, they used kinetic and aging data obtained from hydroprocessing experiments to study the effect of reactor configuration on the cycle length of heavy oil fixed-bed hydroprocessing unit [21].

In order to develop a validated TBR model, kinetic models for all hydrotreating reactions should be developed. However, in the previous models hydrodeasphaltenization reactions (HDA) were excluded. Therefore, Jarullah et al. [22] developed a kinetic model for HDA reactions in TBR. Elizalde and Ancheyta [23] used a three stage deactivation model for simulating the complete period of catalyst deactivation during heavy oil hydrotreating. In addition, they employed a pore plugging model to investigate the deactivation of heavy oil hydrotreating catalysts. Because of the prevalent current trend of oil refiners toward production of diesel fuel with ultra low pollutants, Paz-zavala et al. [24] developed a kinetic model for HDS process to obtain ultra low sulfur diesel in order to be applied to commercial units proving

their capability.

Due to the complexity of modeling the kinetics for some reactions, several studies executed modeling of hydrotreating and different petroleum processing units based on industrial data using commercial simulators such as Aspen HYSYS. Remesat et al. [25] evolved a lumped parameter dynamic model using both Excel and HYSYS for industrial VGO hydrotreater. Du et al. [26] proposed a real component based method for simulation of a diesel hydrotreating process using the software of Unisim Design, which is similar to HYSYS. Said et al. [27] modeled an industrial Penex isomerization unit using Aspen HYSYS Petroleum Refining isomerization reactor model. On the other hand, many studies utilized the commercial software for optimizing the operating conditions of industrial units. Weifeng et al. [28] optimized the catalytic reforming process for an industrial unit using Aspen Plus platform. Al-Lagtah et al. [29] proposed some modifications to an existing plant for gas sweetening process in order to increase its profitability and sustainability using an optimization tool in Aspen HYSYS. Finally, Taqvi et al. [30] enhanced the performance of distillation column for acetone production unit by applying optimization techniques provided in Aspen Plus simulator.

Very little attention was paid in the literature to the application of kinetic modeling and optimization to an existing industrial hydrotreating unit. In this context, we present here a process kinetic model for an existing industrial UOP Coker Distillates Hydrotreating unit using Aspen HYSYS Petroleum Refining Hydroprocessing Bed® module. In addition, the model has been utilized for investigating the effect of different process variables on process performance and for process optimization.

2. Process description

The hydrotreating unit under investigation is designed to treat several petroleum fractions produced by distillation or thermal cracking including straight run and cracked gas oil cuts in order to meet the marketing specifications. This unit is a part of Coker Complex units that consist of two-stage distillation unit where long residue of Land Belayim crude oil is distilled in an atmospheric and vacuum distillation towers to separate all fractions as possible. In addition, short residue is sent to delayed coking unit to generate gas, wild naphtha, cracked middle distillates and coke. All middle distillates are charged to hydrotreating unit, where olefins and aromatics are saturated, and sulfur and nitrogen compounds are eliminated. Hydrotreating units in

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