

INSIGHTS FROM SIMULATIONS AT DIFFERENT SCALES IN RESIDUE HYDROPROCESSING

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Summary

A fixed-bed residue hydroprocessing model was developed accounting for the physical and chemical phenomena occurring at various levels. The reactor model is a heterogeneous three-phase plug flow model, which includes molecular and hindered diffusion inside the catalyst. The catalyst porous structure is represented by Random Spheres, Needles and Coins depending on the catalyst. The use of such catalyst structure models allows to advantageously represent catalyst aging. The reaction network is based on 12 chemical lumps that were further subdivided to track their atomic composition. The model accurately predicts the reactor performances, as well as the influence of catalyst deactivation.

Keywords

Multiscale modeling, multiphase reactors, heavy oil processing.

Introduction

Crude oils contain large fractions of heavy products for which only few commercial outlets exist. Refining processes converting heavy oils into more valuable products, such as gasolines, kerosenes and middle distillates, are therefore vital to a refinery. The heaviest cuts, termed residues, also contain the largest amounts of impurities, which are usually hetero-atom compounds containing sulfur, nitrogen, and/or metals. Fixed bed residue hydrotreating mainly aims at removing these impurities and at increasing the hydrogen content of the hydrocarbon inlet stream. Residue hydroprocessing is carried out at high temperature and under a high hydrogen partial pressure, and with a catalyst promoting a complex network of reactions, amongst which are hydrodemetallization, hydrodesulfurization, hydrodenitrogenation, hydrocracking, and hydrogenolysis reactions. To enable these chemical transformations, the residue feed passes over several fixed adiabatic beds containing different catalysts.¹

The reactivity of a residue feed depends both on the concentration and the nature of the various species.² As even cutting-edge analytical techniques are not able to resolve the complex composition of petroleum residues, a widespread Liquid Chromatography technique is often used to characterize the feed in terms of saturates, aromatics, resins and asphaltenes. The latter are colloid structures whose radius of gyration typically lies between 10 Å and 500 Å.^{3,4} Asphaltenes can therefore only penetrate into the outer layers of porous catalysts. Their penetration is not only governed by molecular and Knudsen diffusion, but also by so-called configurational

diffusion or surface diffusion. Hence, the performances of residue hydrotreating catalysts also strongly depend on their porous texture.

Modeling approach

In this work, the performance of fixed bed residue hydrotreating units is predicted based on a model translating the various physical and chemical phenomena.

The porous structure of the catalysts was represented by Random Spheres, Random Needles and Random Coins models.⁵ The three-phase heterogeneous one-dimensional plug flow model accounts for transport of species by convection. Intraparticle diffusion is represented by Fick's law, but the effective diffusion coefficient has several contributions. Indeed, as the species can have a radius of gyration that is of the same order of magnitude as the pore size, configurational diffusion is explicitly accounted for.⁶

To describe the reactions, the hydrocarbon mixtures were first separated according to their boiling point into a low boiling (<375°C), intermediate boiling (375°C-520°C), and a high boiling (>520°C) fraction. Each fraction was then separated in terms of saturates, aromatics, resins and asphaltenes. In total, 12 chemical lumps are thus represented (gas; light, intermediate and heavy saturates; light, intermediate and heavy aromatics; intermediate and heavy resins; asphaltenes, aggregated asphaltenes, and deposits). To follow the purification reactions, the atomic composition (C, H, S, N, O, Ni and

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V) of each of these 12 lumps was also analyzed and tracked in the model. This finally leads to a reaction network that contains 149 reactions between the 57 subspecies.

In residue hydrotreating, catalyst aging is extremely rapid and run lengths are typically around 10 to 12 months. The build-up of deposited coke and metal sulfides over time strongly affects the catalyst accessibility and pore structure, and hence its activity. The use of Random Spheres, Random Needles and Random Coins models for the catalyst structure allows to advantageously represent catalyst aging. Indeed, the nucleation and growth of solid deposits (metal sulfides, coke) inside the porosity can easily be mimicked by superimposing three random media (fresh catalyst, metal sulfides, coke), and calculate the residual porosity, surface area and average pore diameter from the volumes of coke deposits and of metal sulfides deposits. These parameters then directly influence the catalyst activity (through the surface area), the effective diffusion coefficients of the various species (through the remaining catalyst porosity and average pore size), and the catalyst accessibility (through the percolation threshold porosity of the catalyst).

Results and Discussion

The kinetic parameters were determined by means of a constrained optimization from experimental data obtained on a representative pilot unit. From the statistical analysis and the various simulations, it can be concluded that the model is able to correctly predict the unit operation. Indeed, a good agreement with the experimental data has been obtained, with regard not only to the concentration profiles of the various lumped families but also to the elemental composition of each family.

The simulations also clearly show that significant intraparticle concentration gradients exist for asphaltenes and heavy resins, even at the reactor outlet, illustrating the need to account for intraparticle diffusion when modeling residue hydroprocessing. The predicted intraparticle profiles for the metal deposits (V and Ni) also correspond well to their measured intraparticle profiles.

Catalyst deactivation was also correctly represented. This is illustrated by comparing the simulation results to a 5000-hour pilot plant run. The strength of this model resides in the fact that catalyst deactivation is not simply adjusted by means of empirical deactivation functions, but directly evolves by combining three structure representations (for the fresh catalyst, for metal sulfides, and for coke) based on random media models.

Finally, the full-scale problem was also tackled with this model by simulating an industrial multi-bed adiabatic reactor with inter-reactor quenches and swing reactor operation. These simulation outputs were then compared to real plant data, i.e. the longitudinal weighted average bed temperature profiles and the post mortem analysis of the spent catalysts.

Conclusions

In this work, a model for fixed-bed residue hydrotreating was developed in order to simultaneously predict the yield structure, the atomic composition (in terms of C, H, S, N, O, Ni, V) of the various lumps and the hydrotreating performances (in terms of HDM, HDS, HDN, ...).

Experimentally measured profiles of metals deposited inside catalysts obtained after catalyst life tests indicated that, for this type of feeds, significant intraparticle diffusion of heavy molecules needs to be explicitly taken into account during the model development. Hence, a three-phase heterogeneous one-dimensional plug flow reactor model was selected that included intraparticle transport of the various compounds. The kinetic model uses a two-level description of the hydrocarbon feedstocks and effluents. The first level is directly based on the analytical fractionation method and distinguishes 12 lumps, which are further divided into subspecies based on their elemental analysis. Catalyst deactivation was represented by superimposing three random media (fresh catalyst, metal sulfides, coke), and calculate the residual porosity, surface area and average pore diameter from the volumes of coke deposits and of metal sulfides deposits.

The model accurately predicts the evolution along the reactor of the concentration profiles of the various lumps, the impurities in the total liquid effluent, and the atomic composition of each lump at various operating conditions and for different feeds, while the decrease in activity over time is correctly represented.

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