



Dealing with uncertainties: Sensitivity analysis of vacuum gas oil hydrotreatment



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HIGHLIGHTS

- Main problem: how to quantify uncertainties in model prediction.
- Sobol index to quantify relationship between inputs and output.
- Sobol index to estimate non influent inputs.
- Sobol index shows strong impact of resins and low impact of ppH₂S.
- We apply Sobol indexes to HDN and HDS reactions.

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ABSTRACT

This work applies sensitivity analysis to a kinetic model of hydrotreating processes. The proposed approach is subdivided into several steps: The first step is to build the kinetic model. The second step is to develop a simplified model (meta model) on which easy calculations can be performed in the next step. The third step is to use the meta model to estimate the influence of each input on the model output without Monte Carlo methods which are difficult to manage. Sensitivity analyses are very useful for model comparison and uncertainties estimation.

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1. Introduction

Hydrocracking (HCK) is one of the most versatile of all petroleum refining processes. It usually converts a heavy, low quality feedstock (VGO: vacuum gas oil) into lighter, valuable transportation fuels, contributing significantly to the overall profitability of the refinery [1]. In particular, Mild hydrocracking is a refining process operating at moderate H₂ pressure (40–120 bar) that insures deep hydrotreating (nitrogen and sulfur removal) of VGO-type feedstocks as well as moderate conversions (up to 50 wt%). The scheme of such a process is given in Fig. 1.

Mild Hydrocrackers [2–4] use one or several combinations of non noble metal group VI elements based on supports with no or very low acidity and do not seem to require strong acidic supports such as zeolite based supports. The set of catalysts is determined according to two different criteria: (1) a compromise between activity and selectivity allowing to attain the desired yields. For example, in Europe, the set of catalysts is usually oriented towards the production of middle distillates; (2) a compromise between

cracking activity and industrial cycle length. Indeed, the high operating temperatures of the Mild hydrocracking process to maximize cracking reactions favors the catalysts deactivation, shortening the catalysts' life cycle.

This process may be used to pretreat fluid catalytic cracking (FCC) feedstocks (Fig. 2). In this case, the objective is to improve the quality of the FCC effluents. It is well known that FCC units are an important contributor to the overall sulfur content of the gasoline pool. The Mild HCK pretreatment ensures low sulfur (50–1500 wppm S) and nitrogen contents at the inlet feed of the FCC unit. Therefore, the Mild HCK + FCC association results in the production of low sulfur gasoline (about 10 wppm) without a hydrosulfurization post-treatment. In terms of nitrogen, high organic nitrogen content leads to stronger inhibition of FCC catalysts. For that reason, the pretreatment allows to preserve the zeolite-type FCC catalysts, diminishing the catalyst replacement rate. Moreover, the hydrogenation of the feedstock molecules during Mild HCK pretreatment improves their crackability in FCC units. For all these reasons, the residue fraction (370 °C+) of the Mild HCK units is an optimal feedstock to FCC units [5].

Another usage of the Mild HCK process is the conversion of heavy petroleum fractions into middle distillates to respond to an

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increasing diesel demand in European and Asia markets. This type of process ensures 20–35 wt% conversion of the 370 °C+ fraction. Typically, naphtha (IBP–150 °C) yields range from 5 to 10 wt%, middle distillates (150–370 °C) yields range from 15 to 30 wt% and unconverted oil yields (370 °C+) range from 60 to 80 wt%. The latter can be used as a basis for lubricants. Nowadays, refiners aim to increase vacuum gas oil conversion and consequently, a new generation of catalysts is being developed by the R&D teams, targeting catalysts with increased conversion and hydrodesulfurization activities.

For the purposes of reactor design, process optimization, and catalyst selection, it is necessary to develop kinetic models, in order to predict as accurately as possible the product distributions under hydrocracking conditions. Such a model is based on the choice of a reaction mechanism depending on various parameters (e.g., kinetic constants).

However, hydrocracking models are only approximations of the real process. Therefore, it is important to study the influence of the models input on the response. This is called sensitivity analysis [2]. Two categories of inputs can be considered. First, model parameters are estimated through practical experiences and can be poorly approximated. Sensitivity analysis will tell which parameters are really essential to focus on, and which can be discarded. The estimation process is then simplified and the resulting model improved. Secondly, operating conditions and feed compositions are key variables to the response, and one can examine their relative influence on the outputs.

The aim of this paper is to apply sensitivity analysis on the model of a complete Mild hydrocracker process, in order to qualify the effects of operating conditions on the response. They are very few applications of these techniques in the open literature [6–9]. This article is decomposed as follows:

- Kinetic model description.
- Sensitivity analysis methodology.
- Discussion and application.

The aim is not to focus on the model (which is simple regarding a more complex model [10]) but rather to explain sensitivity analysis and which information could be provided by such analysis.

2. Kinetic modeling

This section is decomposed into a description of the kinetic pathways, followed by the presentation of the reactor model.

2.1. Mechanism description

Even if sulfur and nitrogen characterization is very difficult [11,12] for VGO fraction, the main mechanism for each reaction type can be defined [3] as described in following sections.

2.1.1. Hydrodesulfurization

Fig. 3 shows the commonly accepted mechanisms for hydrodesulfurization (HDS) [13]. The mechanisms pass through two reaction pathways usually called the DDS (direct desulfurization) pathway in which the C–S bond is broken without preliminary hydrogenation of the aromatic ring, and a so-called hydrogenation (HYD) pathway which requires the preliminary hydrogenation of at least one aromatic ring.

It is well known that nitrogen compounds have inhibition effects on these HDS reactions [14,15].

The amount of sulfur can be determined by wavelength dispersive X-ray fluorescence [NF EN ISO 14596], and [NF EN ISO 20884] when the sulfur content is high.

2.1.2. Hydrodenitrogenation

The decomposition of (multi-ring) heterocyclic aromatic N-compounds, the most common nitrogen species in VGO feedstocks, proceeds through a complex reaction network, in which the kinetics are not entirely unraveled yet. There is, however, widespread agreement that the heterocyclic ring hydrogenation is required prior to the breaking of a C–N bond. This applies to both five-membered (e.g., indole, carbazole) and six-membered (e.g., pyridine, quinoline) ring compounds. An example of a hydrodenitrogenation (HDN) mechanism is given for a carbazole molecule in Fig. 4.

For heterocyclic compounds containing two or more adjacent aromatic rings (e.g., quinoline, acridine), it is less clear whether

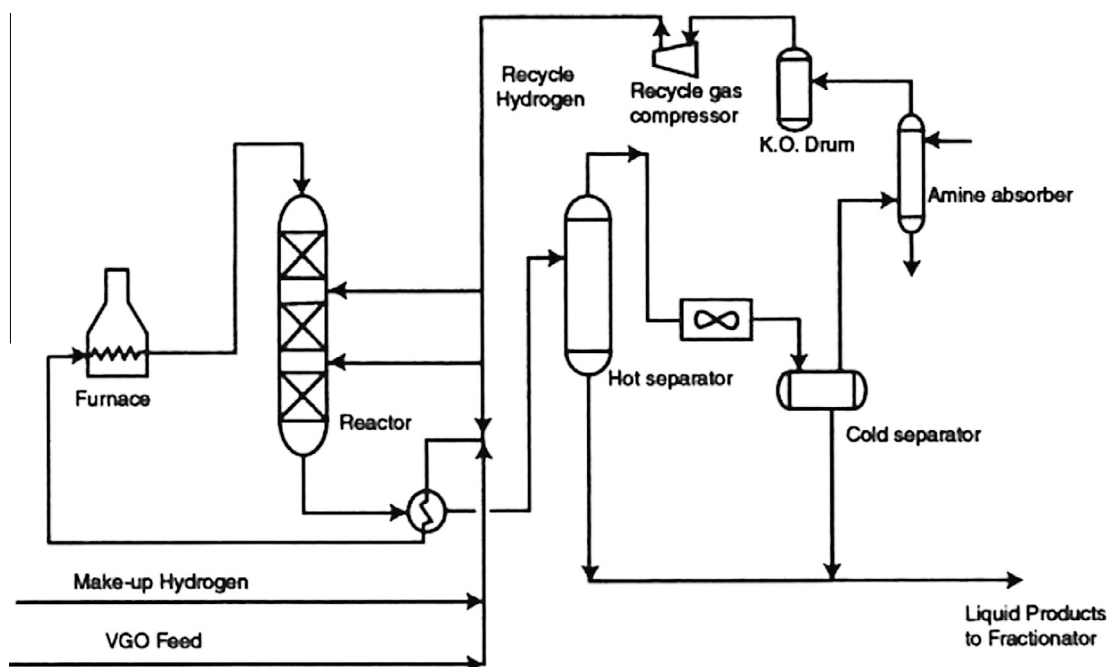


Fig. 1. Process flow diagram of the Mild hydrocracker process [3].

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