



A continuous lumping model for hydrocracking on a zeolite catalysts: model development and parameter identification



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HIGHLIGHTS

- A continuous lumping model was applied to hydrocracking of VGO.
- Experimental data from a pilot plant was used for calibration and validation.
- Good results are obtained for a wide range of operating conditions and feeds.
- A detailed statistical analysis of model parameters is presented.

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ABSTRACT

Process models are a vital tool for the development of industrial hydrocracking units and to drive innovation of process design and novel catalysts. A hydrocracking model, based on the continuous lumping approach, is presented in this work. A zeolite catalyst was used for hydrocracking of pre-treated VGO feeds. The model includes inhibition terms for organic nitrogen and NH_3 gas. A total of 74 data points, from experimental runs in a fixed-bed pilot plant, have been used for parameter identification (52 points) and model validation (22 points). The model has been found to provide a good estimation of total residue (>370 °C cut) conversion and yield structure (naphtha, kerosene and diesel). A statistical analysis of the 12 model parameters, based on the Eigenvectors of the Hessian has been presented. The impact of the individual parameters on the objective function was thus evaluated. This analysis can help guide future refinement of the model.

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1. Introduction

The rapid decline in conventional light crude oil resources [1], combined with the increasing demand for middle distillates (i.e. Kerosene and Gasoil cuts) [2,3] have made Hydrocracking an increasingly attractive option for upgrading of Vacuum Gas Oil (VGO) residue. The VGO cut is characterized by a high True Boiling Point (i.e. high percentage of >370 °C cut) [4]. It frequently contains relatively high amounts of organic nitrogen and sulfur, which are undesirable in the final products (e.g. diesel, fuel oil). The purpose of hydrocracking units is the transformation of VGO to valuable middle distillate fractions, conforming to ever more stringent product quality specifications [5].

The hydrocracking (HCK) process involves the breaking up of large hydrocarbons by β -scission, hydrogenation of aromatic rings,

as well as PCP-isomerization. The removal of organic nitrogen and sulfur by hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reactions are another important function of a HCK unit [5]. A hydrocracking unit often uses a zeolite catalyst with an acid and a metallic site [6]. A good general description of the mechanism is given by Weitkamp [7].

The reaction mechanism of such bifunctional catalysts has been the object of a number of past [8,9] and recent studies [10–16]. Many of these studies are focused on model feeds, such as Fisher–Tropsch wax [14] or *n*-alkane mixtures [15]. Maya residue [17] and Athabasca bitumen derived VGO [16] are among the industrial feedstocks used for model development.

Hydrocracking is considered to be an extremely versatile process [1,7]. A large number of different feedstocks can be converted into a broad range of products by carefully choosing the catalyst and adjusting operating conditions [1,18–20]. Hydrocracking of non-conventional and non-crude feedstocks is becoming an increasingly active area of research. This study is focused on the

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development of a hydrocracking model based on traditional VGO residues.

Even if HCK is a well-established tool in the petroleum refining industry [5], the continuing improvement in analytic techniques and computational capabilities have led to a number of recent developments in this field [5,21,22]. Process modeling, in particular, has been a major factor in advancing the understanding the operation of hydrocracking units [23]. There are two main motivations for developing hydrocracking models: (1) obtaining robust predictions of the performance of HCK units, which can be used to guide process design and optimization, and (2) obtaining a more nuanced understanding of the underlying physico-chemical processes to guide basic research and development of new catalysts and/or process designs.

Accurate and robust simulation of residue (i.e. >370 °C cut) conversion, yield structure in terms of standard cuts, and simulated distillation (SIMDIS) is required by a hydrocracking model. The hydrogen consumption, generation of gases (C3 and C4), as well as a number of product qualities should also be well predicted. An advanced HCK model should be validated for a wide range of operating conditions and for different feeds in order to have the explanatory capabilities. When the tuning parameters for a complex model, including mechanistic considerations as well as empirical aspects, are adjusted for a very restrained database, they are only valid within this limited range. In this case little or no additional information regarding the underlying physico-chemical processes of the system can be gained, regardless of the level of detail of the model. Simple empirical correlations can often give equivalent results than a continuous lumping model within the restrained range of applicability. This work aims to show that a continuous lumping model can be validated for a large range of operating conditions (temperature, contact time, H₂/HC), and feedstocks (residue content, nitrogen content).

Comprehensive reviews of the recent development in hydrocracking models have been compiled by Ancheyta and Elizade [21,24]. A number of different approaches are used, depending on the available data and intended application of the model. Discrete lumping models, which use dedicated correlations for the reactivity of each lump, are among the simplest option. First developed by Qader and Hill [25], these models have been widely used [21,22]. The lumps can represent specific cuts or pseudo components [26]. Continuous lumping models offer a much finer resolution of the feed. They consider the hydrocarbon mixture to be a continuous distribution along an internal coordinate (most commonly True Boiling Point, TBP) [21,22,24,27,28]. A more detailed description of the reaction network can be achieved by decomposition of the feed into a number of lumps, each distributed along TBP [22]. Other modeling approaches include the use of neural networks [29] and microkinetic modeling [30–33]. Using neural networks is an entirely empirical black-box approach, which is not based on an understanding of the underlying chemical kinetics. These powerful models can be used when large amounts of data are available. Microkinetic modeling, such as the single events approach, is based on the reconstruction of the feed into its individual molecules. A large reaction network with thousands of possible reaction pathways is then constructed. These models require a detailed understanding of the chemical kinetics and feed composition. A large amount of computational resources is also required.

The data fitting procedure and statistical analysis of model parameters for a continuous lumping model is presented in this work. The paper is composed of 6 sections. The experimental setup of the pilot plant and the databases is presented in Section 2. Details of the continuous lumping model used here are given in Section 3. This is followed by a description of the parameter fitting procedure, as well as a model evaluation in Sections 4 and 5. A statistical analysis of the model parameters is given in Section 6.

2. Materials & methods

2.1. Process description

Industrial hydrocracking operations are generally a two-step process (R1 + R2). The second step (R2) is considered separately in this study. The main HCK reactor, with a zeolite catalyst follows an hydrotreatment reactor. The first reactor (R1) uses a catalyst designed to remove organic nitrogen and sulfur, hydrogenate aromatic compounds, and remove metallic impurities. These catalysts are much less susceptible to poisoning than the zeolite-based HCK catalysts. Nitrogen- and sulfur-containing compounds, as well as metals are known to inhibit zeolite catalysts [5]. This allows the more fragile zeolite catalyst in the second reactor (R2) to perform the main hydrocracking reaction. The main purpose of the HCK catalyst (R2) is the breaking up of large hydrocarbon molecules contained in the VGO residue, in order to obtain the more valuable middle distillate cuts. Two types of tests were used in the calibration and evaluation databases: (1) pretreatment (R1) and hydrocracking (R2) in a single step, and; (2) separate pretreatment (R1). These two cases are illustrated in Fig. 1.

In the first case, the gases produced in R1 (H₂S, NH₃, hydrocarbon gasses) are carried over in the feed entering R2. The total mass entering R2, with respect to the feed of R1, is equal to the sum of the mass entering two-step process and the hydrogen consumption in R1. The total yield of the two reactors is then equal to the mass of the feed (R1) and the hydrogen consumption in the two reactors (R1 and R2).

In the second case, the gases are separated from the effluent of the pretreatment reactor, which is analyzed and stored for subsequent use in a hydrocracking test. The feed entering R2 is therefore 100% liquid. Aniline and dimethyldisulfide (DMDS) additives are added in order to include the effect of NH₃ and H₂S on the zeolite catalyst. This mass is subsequently subtracted from the effluent, giving a total yield of sum of the mass of the feed (R2) and the hydrogen consumption (excluding H₂ used up in the generation of H₂S from DMDS and NH₃ from Aniline). This setup allows the influence of feed nitrogen content to be studied independent of other feed characteristics.

The sulfur and nitrogen contents in the liquid stream entering R2 are subsequently referred to as S_{R2} and N_{R2}, respectively. The nitrogen and sulfur content entering R1 are referred to as N_{R1} and S_{R1}. In the case of a pretreated feed, the equivalent nitrogen content due to aniline additive is used instead.

2.2. The pilot plant

The experimental runs presented in this study were performed in a pilot unit at IFP Energies Nouvelles, Solaize, France. The hydrocracking step was performed on a commercial catalyst. Various commercial HDT catalysts were used for the pretreatment step. Total catalyst volume in both reactors was 50 cm³. The plant consists of a number of fixed beds, down-flow reactors, designed to mirror the operating conditions in industrial hydrocracking units. Unlike industrial units, which operate in adiabatic mode, the pilot plant operates in isothermal conditions. Temperature is controlled along the reactor. The units were run in continuous operation. Individual mass balances were taken for up to 12 h, after temperatures, pressures, flow rates, and effluent properties were stabilized. A series of mass balances with different operating conditions were thus taken from each experimental run. Each mass balance corresponds to a single experimental point.

Analyses were performed on the feedstocks, the liquid and gaseous effluents, as well as a sample taken on the effluent of the pretreatment reactor (where applicable, see Figs. 1 and 2).

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