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A single events microkinetic model for hydrocracking of vacuum gas oil

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ABSTRACT

The single events microkinetic modelling approach is extended to include saturated and unsaturated cyclic molecules, in addition to paraffins. The model is successfully applied to hydrocracking (HCK) of an hydrotreated Vacuum Gas Oil (VGO) residue in a pilot plant, under industrial operating conditions, on a commercial bi-functional catalyst. The molecular composition of the VGO feed is obtained by reconstruction based on a combination of analytical data (SIMDIS, GCxGC, mass spectrometryspectrometry). The necessary extensions to the single events methodology, which has previously only been applied to much simpler reacting systems (i.e. HCK of paraffins) are detailed in this work. Feeds typically used in the petrochemical industry typically contain a far more complex mixture of hydrocarbons, including cyclic species (i.e. naphthenes & aromatics). A more complex reaction network is therefore required in order to apply a single events model to such feeds. Hydrogenation, as well as endo- and exo-cyclic reactions have been added to the well-known acyclic β-scission and PCP-isomerization reactions. A model for aromatic ring hydrogenation was included in order to be able to simulate the reduction in aromatic rings, which is an important feature of HCK units. The model was then applied to 8 mass balances with a wide range of residue conversion (20–90%). The single events model is shown to be capable of correctly simulating the macroscopic effluent characteristics, such as residue conversion, yield structure, and weight distribution of paraffinic, naphthenic, and aromatic compounds in the standard cuts. This validates the overall model. The single events model provides far more detail about the fundamental chemistry of the system. This is shown in a detailed analysis of the reaction kinetics. The evolution of molecule size (i.e. carbon number), number of saturated/unsaturated rings, or the ratio of branched and un-branched species can be followed along the reactor. This demonstrates the explanatory power of this type of model. Calculations are performed on the IFPEN high performance computing cluster, with parallelization via MPI (message passing interface). This was very useful in order to reduce time consuming problems especially for the parameter fitting step

1. Introduction

A single events microkinetic model is applied to the Hydrocracking (HCK) of a hydrotreated Vacuum Gas Oil (VGO) feed. The single events methodology was first developed in the 1980s by Baltanas et al. (Baltanas et al., 1989), as a method of capturing the fundamental chemistry of the HCK process. A number of studies detailing the application and on-going development of this methodology have since been published (Mitsios et al., 2009; Guillaume et al., 2011; Schweitzer et al., 1999; Froment, 2005; Valery et al., 2007; Martens, 1999; Laxmi Narasimhan et al., 2004; Lozano-Blanco et al., 2010; Kumar and Froment, 2007). These studies are essentially limited to long chain alkanes. Industrial feedstocks contain, however, a far more complex mixture of hydrocarbons, including (poly-) cyclic species such as naphthenes, aromatics, and naphtheneo-aromatics. A typical hydrotreated VGO feed contains, 20–30% w/w paraffins, 50–80% w/w naphthenes, and 10–20% w/w aromatics. The high concentration of cyclic shows that the extension to the single events model is mandatory for the simulation of such feeds. This must be taken into account by a microkinetic model intended to be useful for simulation of industrial HCK units. The model presented here is an extension of previous single events models to saturated and unsaturated cyclic hydrocarbons, and the specific reactions associated with such molecules. The model is shown to be able to simulate HCK of a typical hydrotreated VGO feed in a pilot plant at industrial operating conditions.

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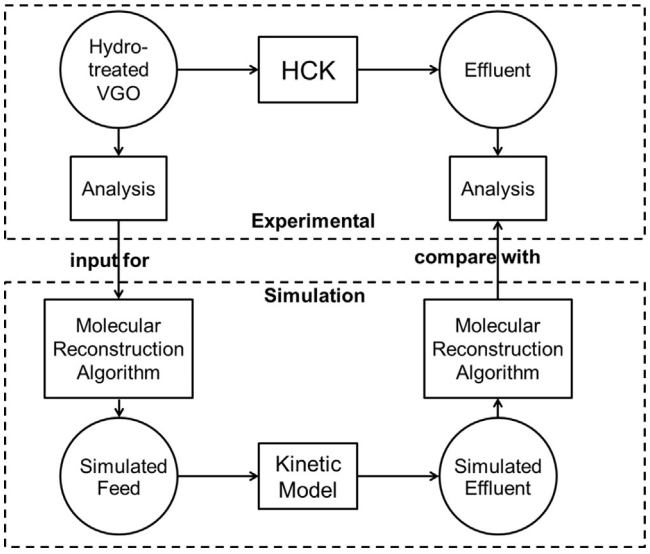

Fig. 1. Outline of the model strategy used in this work.

A detailed reaction network, based on the decomposition of the feed according to carbon number and 19 chemical families is constructed. The model is then used to simulate hydrocracking on a commercial catalyst industrial operating conditions, in a pilot plant. The model strategy is outlined in Fig. 1. The molecular reconstruction of the feed, based on experimental measurements is the input of the kinetic model. The macroscopic effluent characteristics are then reconstructed from the individual molecules from single events simulation output. This can then be compared to the experimentally measured macroscopic effluent characteristics.

The motivations for the application of a microkinetic model to a real hydrocracking process is to capture the fundamental chemistry of this complex system in better detail than can be provided by, for example, continuous- or discrete lumping techniques. Moreover, in order to reduce time consuming problems, a dedicated implementation to super calculator is required.

This paper is structured as follows: The hydrocracking (HCK) process, catalyst, as well as an overview of recent advances in HCK modelling is presented in Section 2. The molecular library and feed reconstruction algorithm is outlined in Section 3. The methodology of the single events microkinetic model is described in Section 4. The set-up of the pilot plant and the available experimental data is briefly presented in Section 5.1. The use of high performance computing is described in Section 5.2. The simulation results are given in the Section 6. This final section is divided as follows: Section 6.1 outlines the kinetic parameter identification, Sections 6.2 and 6.3 focus on the validation of macroscopic effluent characteristics, and Section 6.4 gives a detailed insight into reaction kinetics. Concluding remarks are provided in Section 7.

2. The hydrocracking process

2.1. Process description

Hydrocracking is a well-established, flexible technology for the processing of petrochemical feedstocks into high-quality products (Ancheyta et al., 2005; Rana et al., 2007; Choudhary and Saraf, 1975; Ward, 1993). The increasing interest for hydrocracking unit in today's oil refining industry is explained by the continuously growing demand of middle distillates with excellent product quality, coupled with the depletion of traditional crude oil resources (Ward, 1993; Mohr et al., 2015). This process allows to convert heavy, low-value fractions such as Vacuum Gas Oil (VGO) into lighter and more valuable middle distillates (kerosene and diesel) or naphtha cuts.

A two-step process is generally used in industrial hydrocracking units (Rana et al., 2007; Choudhary and Saraf, 1975; Becker et al., 2015): A first hydrotreatment (HDT) step and a second cracking (HCK) step. The HDT step essentially serves to remove heteroatoms (Nitrogen, Sulfur...) from the VGO feed in order to satisfy product quality constraints and to prevent nitrogen to act as a poison for the more sensitive HCK catalyst which cracks heavy molecules.

The hydrotreated feed of the HCK reactor is assumed to be essentially free of heteroatoms and thus composed exclusively of hydrocarbon molecules. Nevertheless this still amounts to a far larger number of species than in a chemical reactor operating with relatively pure feeds and limited numbers of potential reactions. The purpose of this work is to establish a single events model for the HCK reactor. This can be considered as a step on the way to develop a complete model, including heteroatoms. Only the second step in the two-step setup is therefore simulated.

Hydrocracking experimental runs were performed in IFPEN pilot plant. The HDT and HCK steps are performed separately, according to the scheme presented in Fig. 2. This setup allows detailed analyses to be performed on the pre-treated feed (Becker et al., 2015). The same feed can then be used in different HCK runs. It is important to note that the gases produced in the first reactor are separated. Ammonia gas must therefore be added to the HCK reactor in order to simulate the effect of carryover of this gas that would occur in an industrial unit (in that case, aniline is used which rapidly breaks down into NH3 and cyclohexane gas). A more detailed description of the HCK process used in this study can be found in (Guillaume et al., 2011; Becker et al., 2015; Becker et al., 2016).

2.2. The hydrocracking catalysts

Hydrocracking is a catalytic cracking process, which is performed at high temperatures (up to 450 °C) and at high hydrogen pressures (200 bar) on a bi-functional catalyst (i.e. including an acidic and a metallic functionality) (Ward, 1993; Marcilly Christian, 2003; Weitkamp, 2012; Froment, 2014). The elementary reactions

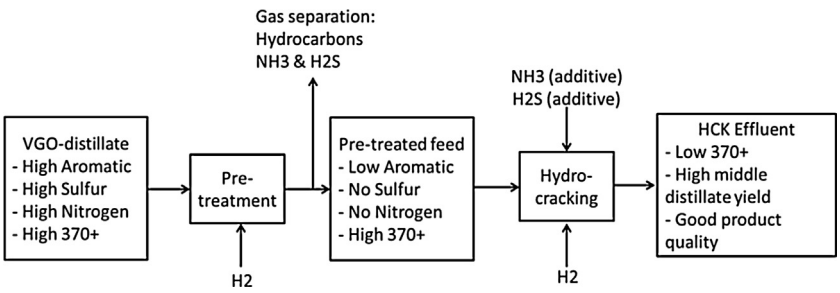

Fig. 2. Schematic representation of the two step hydrocracking process with intermediate storage/analysis of the pre-treated feed.