Comparing hydrocracking models: Continuous lumping vs. single events

P.J. Becker [a], N. Serrand [a], B. Celse [a,*], D. Guillaume [a], H. Dulot [b]

[a] IFP Energies Nouvelles, Rond Point de l'échangeur de Solaize, BP 3, 69360 Solaize, France
[b] AXENS, 89, Boulevard Franklin Roosevelt, BP 50802, 95208 Rueil-Malmaison, France

HIGHLIGHTS

- Comparison of single events microkinetic and continuous lumping hydrocracking models.
- Continuous lumping model is more accurate for simulation of yield structure.
- Single events model provides detailed kinetic data.
- The conversion and cracking/isomerization product distributions are traced.

ARTICLE INFO

ABSTRACT

Development of models for industrial hydrocrackers has received a great amount of attention by the scientific community over the past decades. Two fundamentally different modelling approaches are compared in this paper: a continuous lumping model with three families (paraffins, naphthenes, and aromatics) and a single events microkinetic model. The aim is to demonstrate the differences in the capabilities of the two modelling frameworks. Both models are capable of simulating experimental data from hydrocracking of a pre-treated Vacuum Gas Oil in a pilot plant at industrial conditions. The continuous lumping model provides better results of the macroscopic effluent characteristics, such as yield structure and PNA (Paraffin, Naphthene, Aromatic) distribution in the middle distillate cut. It requires only the feed SIMDIS (Simulated Distillation) and PNA composition to be known. The single events model, on the other hand, provides information which is not available in a simple continuous lumping model. An analysis of the reaction kinetics of paraffins and mono-naphthenes is performed to demonstrate this aspect. The single events model is far more complex and computationally expensive than the continuous lumping model. In conclusion, the two approaches should be considered complementary rather than competitive. In conjunction, they can be used to balance the drawbacks of each individual modelling approach.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Transformation of heavy crude oil into more valuable light (naphta) and middle distillates (gasoil and kerosene) is becoming increasingly important for the petrochemical industry. A recent study by Mohr et al. [1] states that production of conventional crude oil has been constant, while there has been a strong increase in unconventional (i.e. heavier) sources. These unconventional crudes are characterized by a very high residue (>370 °C cut) content, high aromatic content, and high concentration of impurities (e.g. nitrogen, sulphur, and metals) [2]. The increasing demand of middle distillates, particularly by developing countries, as well as the increasingly stringent quality requirements drives the need

for increasingly sophisticated refining technology. Catalytic hydrocracking (HCK) is a widely used process capable of a high rate of conversion of residue to high quality middle distillates [3–6].

The capability of accurately modelling the HCK process is essential to take full advantage of the versatility of the process in terms of feed characteristics and desired yield and cost of a given unit. Chemical engineers will typically use kinetic models to determine the optimal design and operating conditions of a HCK unit for a given job [7]. The principal difficulty of modelling HCK processes is the very complex nature of the feeds and effluents, compared to more pure systems encountered elsewhere in the chemical industry. A large number of relatively simple discrete and continuous lumping models have been proposed, the most recent can be found in [8–17]. More recently, the use of more complex and fundamental microkinetic models to simulate HCK has generated considerable interest by the research community [18–26]. The two modelling

approaches are fundamentally different: The traditional lumping models take their starting point in the macroscopic level (i.e. measurable product properties) and derive a set of kinetic equations from there. Microkinetic models work their way up from the molecular level, by deriving the kinetic equations from the chemical reactions between individual molecules. In simple, pure systems, containing a few of chemical species, the two approaches often converge in the same (or in the least very similar) set of equations. For models concerned with heavy petroleum fractions containing 100 s or 1000 s of chemical species it is not possible to draw out a complete reaction network by hand [2]. Even modern computational tools often reach their limit, since the size of the reaction network increases exponentially with the carbon number.

Lumped and microkinetic HCK models have distinct set of advantages and drawbacks. Literature comparing different HCK models is scarce. Ancheyta [16] provides a review of recent advances in HCK modelling and compares the performance and kinetic parameters of four lumping models (two discrete, one based on pseudo components, and one continuous). This paper specifically states the feed dependence of model parameters as a major drawback of continuous lumping models. In theory, microkinetic models have no such dependence. The objective of this work is to provide a comprehensive comparison between the Single Events Microkinetic (SMEK) and the Continuous Lumping approaches in HCK modelling. The intent is not to merely compare the two models with respect to the accuracy of the simulation results, but rather to highlight the inherent differences and showcase the different capabilities. This is meant to serve as a guideline to help the reader chose the appropriate model based on the available experimental data, the required detail of the simulation results, and the specific application (e.g. fundamental research/ process design).

2. Background

2.1. The hydrocracking process

The hydrocracking process studied in this work is a two-step process, which is often used in industrial units [3,27]. The hydrotreatment (HDT) reactor uses a more robust catalyst, which essentially serves to remove heteroatoms from the VGO feed in order to satisfy product quality constraints and avoid poisoning of the more delicate zeolite-based HCK catalysts [3]. The second, hydrocracking (HCK) reactor uses a commercial zeolite catalyst with a carefully selected balance of acid and metallic sites. The HCK is generally run at high temperatures (up to 400 °C) and at high hydrogen pressures (140 bar) on a bi-functional catalyst. The chemistry of the elementary steps occurring on the acid and metallic sites are described extensively in the literature, e.g. [4,5,26,28]. Only the second (i.e. HCK) step is simulated here to avoid the additional difficulty of including organic species with nitrogen or sulphur heteroatoms in the models.

2.2. Hydrocracking models

Hydrocracking models have evolved significantly over the last few decades. An extensive review of the existing models was done by Ancheyta et al. [16]. An increase in the complexity of the models proposed by the scientific community can be observed. A number of kinetic models consisting of a limited number (generally less than 10) lumps have been proposed (see for example [6,15,29]). These models are constructed to be extreme over-simplifications of a reacting system with 100–1000 s of different molecular species and 10^5–10^6 individual reactions. They can be used to simulate a limited number of quantities important to the operator and/or

designer of a HCK unit, such as gasoil yield. The amount of information that can be obtained from discrete lumping models is somewhat limited. Where a distillation curve is required it must be interpolated from a low number of lumps. The number of kinetic parameters to be identified increase exponentially with the number of lumps. The limiting case of this approach would be one lump for each individual chemical species, which is clearly not feasible.

Continuous lumping models have been developed in order to address these issues (see for example [9,16,19,30–33]). The hydrocarbon mixture is considered in terms of a continuous distribution (typically in terms of boiling point) rather than being made up of discrete entities. The reactivity is then defined as a continuous function. This allows a very fine resolution of the distillation curve without an exponential increase in the number of parameters. It is also possible to combine the discrete and continuous lumping approaches by defining more than one continuous distribution [10].

The lumping based modelling approaches take their starting point in the macro-scale, with a requirement to simulate a yield distribution, distillation curve, or a specific effluent property. Microkinetic models, on the other hand, are developed from the molecular scale, by considering the chemistry of the reacting system. The two approaches converge relatively quickly for chemical systems with 10s of relatively pure species. The development of microkinetic models for HCK of heavy petroleum fractions is driven by the availability of increasingly sophisticated analytical techniques (e.g. [34–36]) and increasing computational capabilities. Computational algorithms have been developed to reduce the size of the reaction networks without loss of information. The single event micro kinetic modelling method was originally developed by Froment et al. [37–42]. The single events coefficients [20,23] are calculated for each individual reaction, before a rigorous re-lumping is performed in order to reduce the size of the network without loss in information. Algorithms have been proposed for hydrocracking [38,43], reforming [44], isomerization [22], alkylation [45]. However, the original re-lumping method remains unfeasible for application to large networks, even with current computational capabilities [46,47]. Two alternative methods exist. The first one is based on a lateral chain decomposition. It was developed by Valery [18,20,25]. The second is based on structural classes. It was developed by Martens & Marin [43].

3. Materials & methods

3.1. Experimental data

Hydrocracking experimental runs were performed in the IFPEN pilot plant. The HDT and HCK steps are performed separately. This setup allows detailed analyses on the pre-treated feed, which are necessary to perform the molecular reconstruction of the feed for the SMEK model [25,26]. The same pre-treated Vacuum Gas Oil (VGO) feed is used in different runs. It is important to note that the gases produced in the first reactor are separated in this set up. Ammonia (NH_3) gas has a noted inhibition effect on the zeolite catalyst. It must therefore be introduced to the HCK reactor, in the form of an additive, in order to simulate the effect of carryover of this gas that would occur in an industrial unit. A more detailed description of the HCK process used in this study can be found in [12].

3.2. Continuous lumping model

A continuous lumping model, with distinction between three families (paraffins/naphthenes/aromatics) is used to evaluate the performance of the single events model. The hydrocarbon mixture