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# A Continuous Lumping Model for Hydrocracking on a Zeolite Catalysts: Model Development and Parameter Identification

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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 (ie.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  $\beta$ -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].

27 Hydrocracking of non-conventional and non-crude feedstocks is becoming an increasingly active area of research. This  
28 study is focused on the development of a hydrocracking model based on traditional VGO residues.

29 Even if HCK is a well-established tool in the petroleum refining industry [5], the continuing improvement in analytic  
30 techniques and computational capabilities have led to a number of recent developments in this field [5,21,22]. Process  
31 modeling, in particular, has been a major factor in advancing the understanding the operation of hydrocracking units  
32 [23]. There are two main motivations for developing hydrocracking models: 1) obtaining robust predictions of the perfor-  
33 mance of HCK units, which can be used to guide process design and optimization, and 2) obtaining a more nuanced un-  
34 derstanding of the underlying physico-chemical processes to guide basic research and development of new catalysts  
35 and/or process designs.

36 Accurate and robust simulation of residue (i.e.  $>370^{\circ}\text{C}$  cut) conversion, yield structure in terms of standard cuts, and  
37 simulated distillation (SIMDIS) is required by a hydrocracking model. The hydrogen consumption, generation of gases  
38 ( $\text{C}_3$  &  $\text{C}_4$ ), as well as a number of product qualities should also be well predicted. An advanced HCK model should be  
39 validated for a wide range of operating conditions and for different feeds in order to have the explanatory capabilities.  
40 When the tuning parameters for a complex model, including mechanistic considerations as well as empirical aspects, are  
41 adjusted for a very restrained database, they are only valid within this limited range. In this case little or no additional  
42 information regarding the underlying physic-chemical processes of the system can be gained, regardless of the level of  
43 detail of the model. Simple empirical correlations can often give equivalent results than a continuous lumping model  
44 within the restrained range of applicability. This work aims to show that a continuous lumping model can be validated for  
45 a large range of operating conditions (temperature, contact time,  $\text{H}_2/\text{HC}$ ), and feedstocks (residue content, nitrogen con-  
46 tent).

47 Comprehensive reviews of the recent development in hydrocracking models have been compiled by Ancheyta and  
48 Elizade [21,24]. A number of different approaches are used, depending on the available data and intended application of  
49 the model. Discrete lumping models, which use dedicated correlations for the reactivity of each lump, are among the  
50 simplest option. First developed by Qader and Hill [25], these models have been widely used [21,22]. The lumps can repre-  
51 sents specific cuts or pseudo components [26]. Continuous lumping models offer a much finer resolution of the feed.  
52 They consider the hydrocarbon mixture to be a continuous distribution along an internal coordinate (most commonly  
53 True Boiling Point, TBP) [21,22,24,27,28]. A more detailed description of the reaction network can be achieved by decom-  
54 position of the feed into a number of lumps, each distributed along TBP [22]. Other modeling approaches include the use  
55 of neural networks [29] and microkinetic modeling [30-33]. Using neural networks is an entirely empirical black-box

56 approach, which is not based on an understanding of the underlying chemical kinetics. These powerful models can be  
57 used when large amounts of data are available. Microkinetic modeling, such as the single events approach, is based on the  
58 reconstruction of the feed into its individual molecules. A large reaction network with thousands of possible reaction  
59 pathways is then constructed. These models require a detailed understanding of the chemical kinetics and feed composi-  
60 tion. A large amount of computational resources is also required.

61 The data fitting procedure and statistical analysis of model parameters for a continuous lumping model is presented in  
62 this work. The paper is structured as follows: The experimental setup of the pilot plant and the databases is presented in  
63 section 2. Details of the continuous lumping model used here are given in section 3. This is followed by a description of  
64 the parameter fitting procedure, as well as a model evaluation in sections 4 and 5. A statistical analysis of the model pa-  
65 rameters is given in section 6.

## 66 2. Materials & Methods

### 67 2.1 Process Description

68 Industrial hydrocracking operations are generally a two-step process ( $R_1 + R_2$ ). The second step ( $R_2$ ) is considered sepa-  
69 rately in this study. The main HCK reactor, with a zeolite catalyst follows an hydrotreatment reactor. The first reactor ( $R_1$ )  
70 uses a catalyst designed to remove organic nitrogen and sulfur, hydrogenate aromatic compounds, and remove metallic  
71 impurities. These catalysts are much less susceptible to poisoning than the zeolite-based HCK catalysts. Nitrogen- and  
72 sulfur-containing compounds, as well as metals are known to inhibit zeolite catalysts [5]. This allows the more fragile  
73 zeolite catalyst in the second reactor ( $R_2$ ) to perform the main hydrocracking reaction. The main purpose of the HCK  
74 catalyst ( $R_2$ ) is the breaking up of large hydrocarbon atoms contained in the VGO residue, in order to obtain the more  
75 valuable middle distillate cuts. Two types of tests were used in the calibration and evaluation databases: 1) pretreatment  
76 ( $R_1$ ) and hydrocracking ( $R_2$ ) in a single step, and; 2) separate pretreatment ( $R_1$ ). These two cases are illustrated in Figure 1

77  
78 In the first case, the gases produced in  $R_1$  ( $H_2S$ ,  $NH_3$ , hydrocarbon gasses) are carried over in the feed entering  $R_2$ . The  
79 total mass entering  $R_2$ , with respect to the feed of  $R_1$ , is equal to the sum of the mass entering two-step process and the  
80 hydrogen consumption in  $R_1$ . The total yield of the two reactors is then equal to the mass of the feed ( $R_1$ ) and the hydro-  
81 gen consumption in the two reactors ( $R_1$  and  $R_2$ ).

82 In the second case, the gases are separated from the effluent of the pretreatment reactor, which is analyzed and stored  
83 for subsequent use in a hydrocracking test. The feed entering R<sub>2</sub> is therefore 100% liquid. Aniline and dimethyldisulfide  
84 (DMDS) additives are added in order to include the effect of NH<sub>3</sub> and H<sub>2</sub>S on the zeolite catalyst. This mass is subse-  
85 quently subtracted from the effluent, giving a total yield of sum of the mass of the feed (R<sub>2</sub>) and the hydrogen consump-  
86 tion (excluding H<sub>2</sub> used up in the generation of H<sub>2</sub>S from DMDS and NH<sub>3</sub> from Aniline). This setup allows the influence  
87 of feed nitrogen content to be studied independent of other feed characteristics.

88 The sulfur and nitrogen contents in the liquid stream entering R<sub>2</sub> are subsequently referred to as S<sub>R<sub>2</sub></sub> and N<sub>R<sub>2</sub></sub>, respec-  
89 tively. The nitrogen and sulfur content entering R<sub>1</sub> are referred to as N<sub>R<sub>1</sub></sub> and S<sub>R<sub>1</sub></sub>. In the case of a pre-treated feed, the  
90 equivalent nitrogen content due to aniline additive is used instead.

## 91 2.2 The Pilot Plant

92 The experimental runs presented in this study were performed in a pilot unit at IFP Energies Nouvelles, Solaize, France.  
93 The hydrocracking step was performed on a commercial NiMoP-zeolite catalyst. Various commercial HDT catalysts were  
94 used for the pretreatment step. Total catalyst volume in both reactors is 50 cm<sup>3</sup>. The plant consists of a number of fixed  
95 beds, down-flow reactors, designed to mirror the operating conditions in industrial hydrocracking units. Unlike industrial  
96 units, which operate in adiabatic mode, the pilot plant operates in isothermal conditions. Temperature is controlled along  
97 the reactor. The units were run in continuous operation. Individual mass balances were taken for up to 12 hours, after  
98 temperatures, pressures, flow rates, and effluent properties were stabilized. A series of mass balances with different oper-  
99 ating conditions were thus taken from each experimental run. Each mass balance corresponds to a single experimental  
100 point.

101 Analyses were performed on the feedstocks, the liquid and gaseous effluents, as well as a sample taken on the effluent  
102 of the pretreatment reactor (where applicable, see Figure 1 and Figure 2). The most relevant measurements to this study  
103 were the analysis of the feed sulfur and nitrogen contents, the partial pressures of NH<sub>3</sub>, H<sub>2</sub>S, and H<sub>2</sub> gasses, as well as the  
104 simulated distillation.

## 105 2.3 The Calibration & Validation Databases

106 A calibration database, consisting of 52 mass balances, was compiled. Feed characteristics and operating condition were  
107 chosen to correspond to the ones encountered in industrial hydrocracking units. This database was used for the identifi-  
108 cation of the empirical parameters in the continuous lumping model. A validation database, consisting of an additional 22

109 mass balances was used to validate the model performance. The feed nitrogen and sulfur content of the two databases is  
110 shown in Figure 3. Different feeds of Iranian or Arabian origin were used at varying levels of pretreatment (R<sub>1</sub>). For about  
111 half (n=31) of the experimental runs, pretreatment and hydrocracking were performed in a single step, corresponding to  
112 Figure 1. The remaining runs (n=43) were performed in separate steps, corresponding to Figure 2.

113 The range of the main operating conditions, temperature (°C), hydrogen to hydrocarbon ratio (H<sub>2</sub>/HC, StdL/L), and  
114 Liquid Hourly Space Velocity (LHSV, h<sup>-1</sup>) is given in Figure 4. The residue (>370°C) cut in the feed of the zeolite catalytic  
115 bed (R<sub>2</sub>) and its conversion,  $X_{370+} = 100 * (1 - Y_{370+,out} / Y_{370+,in})$  are given in Figure 5 to give an overview of the performance of  
116 the experimental runs.

117 The range of the residual organic nitrogen in the feed is 0 – 154 ppm. Four runs in the calibration database had con-  
118 tained no detectable organic nitrogen; these are not shown in Figure 3 because of the log scale. The sulfur content is not  
119 used in the modeling because it has been found to have negligible influence on hydrocracking reactions on a zeolite cata-  
120 lyst. The NH<sub>3</sub> entering R<sub>2</sub>, due to the feed nitrogen content of the pretreatment reactor or the aniline additive was varied  
121 between 570 and 2800 ppm, with one run performed at a very high value of 5000 ppm. The nitrogen and sulfur content in  
122 the R<sub>1</sub> and R<sub>2</sub> feeds of the validation database are within the range of the validation database. The variations in the feeds  
123 must be taken into account by the model. Using a continuous rather than a discrete lumping approach allows the full  
124 distribution (SIMDIS) of the feed rather than a limited number of lumps to be used as the model input.

125 Most tests were performed at a standard ratio of H<sub>2</sub> gas to hydrocarbon flowrates (H<sub>2</sub>/HC) of 1000 L/L (std) and a total  
126 pressure of 140 bar. Four runs in the calibration database were performed at 100 bar, while four runs in the validation  
127 database were performed at 160 bar. The temperature and LHSV were varied between 370 – 401°C and 1.3 – 4.2 h<sup>-1</sup> in the  
128 calibration database. The validation tests generally fall within the same range, with the exception of four runs with a  
129 LHSV of 0.9 h<sup>-1</sup>, and one test at a very low temperature of 362°C.

130 The residue (>370°C cut) of the feed of R<sub>2</sub> falls in a relatively narrow range of between 67 – 84 %, with two validation  
131 tests at around 50 %, corresponding to very high levels of pretreatment. The conversion (X<sub>370+</sub>), on the other hand, covers  
132 the complete range that can be achieved in a hydrocracking reactor, i.e. up to 100 %.

133 Measurements for the composition of the residue (>370°C) cut of the calibration feeds (R<sub>2</sub>), in terms of paraffin (P),  
134 naphthene (N) and aromatic (A) compounds are available for the pretreated feeds (see Figure 2). This shows that the com-  
135 position of the feeds used in this study does not vary very much. The residue cut of the feeds have an aromatics content of  
136 10 to 37 %, with most feeds close to 30%.



138

### 139 3. Model Development

#### 140 3.1 The Continuous Lumping Framework

141 The modeling framework considered the hydrocarbon mixture to be a continuous distribution of true boiling point  
142 (TBP). The reactivity of the components follows a curve described as a function of normalized TBP  $\theta$ . Hydrocarbons be-  
143 low 8 carbon atoms (TBP  $\approx 124^\circ\text{C}$ ) are assumed to undergo no further cracking, while cracking of very heavy hydrocarbons  
144 ( $>700^\circ\text{C}$ ) is considered to be constant and thus independent of TBP. The normalized TBP is defined as:

145

146

$$\theta = \frac{TBP - T_{min}}{T_{max} - T_{min}} \quad (1)$$

147 **Where:**

**$TBP$**  True Boiling Point ( $^\circ\text{C}$ )

**$T_{min}$**   $-7.6^\circ\text{C}$  (TBP of  $\text{C}_4\text{H}_{10}$ )

**$T_{max}$**   $700^\circ\text{C}$

148

149

150 It is important to note that the main cracking mechanism is  $\beta$ -scission of saturated hydrocarbon chains or cycles.  $\beta$ -  
151 scissions on a straight chain result in two smaller molecules with lower boiling points. For endo-cyclic  $\beta$ -scissions of cy-  
152 cloalkanes (i.e. ring opening), a single, saturated alkane chain is formed. This results in a change in TBP, but no reduction  
153 in size of the molecule. However, a number of different reaction types occur during the hydrocracking process. Isomeriza-  
154 tion reactions change the branching degree of a hydrocarbon, which can increase or decrease the TBP of the reaction  
155 product. Aromatic compounds are hydrogenated, forming saturated cycloalkanes (naphthenes). Hydrogenation of aro-  
156 matic rings is also accompanied by a decrease in boiling point.

157 These reactions are not explicitly modeled in the continuous lumping model presented here. The set of reactions, caus-  
158 ing a decrease in the TBP of the mixture are lumped together to give an apparent reaction rate. A more detailed, multi-  
159 family approach, which treats the reaction pathways between aromatic, naphthene, and paraffins explicitly, has been pre-  
160 sented by Becker et al. [22]. Fitting the parameters of this model requires detailed knowledge of the feed and effluent



161 composition.. Such analyses are rarely available in an industrial context. A model capable of predicting the composition of  
162 the effluent is therefore of limited usefulness for the hydrocracking units design and optimization. However, they are  
163 useful in a research and development context. They allow the characterization of the chemical reaction pathways and  
164 activity of a catalyst. This can lead to a better understanding of the underlying phenomena which can consequently be  
165 used to guide future developments.

166 The model presented here has been developed to capture the effect of the main operating parameters and feed condi-  
167 tions in order to predict the yield structure of the hydrocracker.

168

170 **3.2 The Model Equations**

171 The feed simulated distillation (SIMDIS) is a cumulative mass distribution. The associated continuous distribution,  $c(\theta, t)$ ,  
 172 can be split up into a number of intervals  $i$ , with  $\Delta\theta_i = [\theta_{i-}, \theta_{i+}]$ , with  $\theta_{i-} < \theta_{i+}$ . The discrete concentration in each inter-  
 173 val,  $C_i$ , is given by:

$$C_i = \int_{\theta_{i-}}^{\theta_{i+}} c(\theta, t) d\theta \quad (2)$$

174 Each interval is represented by  $\theta_i$ . The mass balance for each interval  $i$  is:

$$\frac{\Delta C_i}{\Delta t} = -R_{i,out} + R_{i,in} \quad (3)$$

175 The mass being eliminated from the interval  $i$ ,  $R_{i,out}$  is due to molecules being cracked. This results in a lower TBP. The  
 176 mass  $R_{i,in}$  being added to the interval  $i$ , is due to the cracking of heavier hydrocarbons (i.e. in classes with  $\theta_j > \theta_i$ ). The mass  
 177 of hydrocarbons resulting from a cracking reaction, which fall in the  $\Delta\theta_i$  interval, i.e. the  $R_{i,out}$  term, is added to the mass  
 178  $C_i$ .

179 A set of partial differential equations for the hydrocracking reaction can be constructed for the continuous mass distri-  
 180 bution  $c(\theta, t)$ , given in equation (2). Here, the continuous elimination and creation terms are denoted  $r_{out}$  and  $r_{in}$  respec-  
 181 tively.

$$\frac{\partial c(\theta, t)}{\partial t} = -r_{out}(\theta, t) + r_{in}(\theta, t) \quad (4)$$

182 An expansion of the elimination ( $r_{out}$ ) and generation ( $r_{in}$ ) terms leads to:

$$\begin{aligned} & \frac{\partial c(\theta, t)}{\partial t} \\ &= -k_{\mathbf{T}} f_X(\theta) I_N(t) C(\theta, t) \\ &+ \int_{\theta}^{\infty} k_{\mathbf{T}} f_X(\theta) I_N(t) C(\theta, t) g(\theta, \theta^*) d\theta^* \end{aligned} \quad (5)$$

183 Where:

$c(\theta, t)$  Mass fraction at TBP  $\theta$ , and time  $t$

$f_X(\theta)$  Reactivity function

$I_N$	Nitrogen inhibition term
$k_T$	Pre-factor at temperature T
$g(\theta, \theta^*)$	Yield distribution function

184

185 The yield distribution,  $g(\theta, \theta^*)$ , and reactivity function,  $f_x(\theta)$ , do not change along the reactor (for isothermal operation)  
 186 and are therefore calculated *a priori*.

187 A gamma function was chosen for the reactivity function and a beta distribution was chosen for the yield distribution.

188 These two functions are very flexible regarding the shapes they can take [22]. They were chosen over the mode common  
 189 Gaussian and exponential distribution to give additional degrees of freedom to the model. The functions are given in  
 190 equations ( 4) and ( 5) respectively Both functions take two tuning parameters.

$$f(\theta) = \theta^A e^{-B\theta} \quad (6)$$

$$g(n, n^*) = \left(\frac{n}{n^*}\right)^{\alpha_y-1} \left(1 - \frac{n}{n^*}\right)^{\beta_y-1} \quad (7)$$

191 Where:

$n$	Number of carbon atoms in compound undergoing cracking
$n^*$	Number of carbon atoms in cracking product
$\alpha_y, \beta_y$	Model parameters for yield distribution
$A, B$	Model parameters for reactivity

192 The yield distribution is defined in terms of carbon numbers (n), rather than TBP ( $\theta$ ) in order to ensure mass conserva-  
 193 tion without an additional normalization term. The model equation (3), however, is defined in terms of TBP ( $\theta$ ). The  
 194 transformation of carbon number to TBP,  $n = f(\theta)$ , is performed according to the TBP of normal paraffins.

195 An Arrhenius term was included in the pre-factor ( $k_T$ ) to account for the effect of temperature variations.

$$k_T = k_0 \exp \left[ -\frac{E_a}{R_g} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (8)$$

196 With:

$k_0$	Pre-factor,model parameter
$E_a$	Activation energy,model parameter (in kJ mol <sup>-1</sup> )
$T$	Reaction temperature (in K)
$T_{ref}$	Reference temperature (in K)

$R_g$  Gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>)

197 The continuous expression (equation 3) is discretized at equally spaced TBP intervals of 5°C. The resulting set of ODEs  
198 is solved by the well-known LSODE solver. The model was implemented in object-oriented FORTRAN.

### 199 3.3 Hydrogen Consumption

200 The total mass flowrate of the effluent is higher than the mass flowrate of the (HCK) feed because of the hydrogen add-  
201 ed in process. Estimation of the hydrogen consumption is necessary in order to determine the total yield of the hy-  
202 drocracking reaction. Two hydrogen atoms (i.e. one H<sub>2</sub>) are added in each β-scission reaction. The total number of crack-  
203 ing reactions is estimated via a correlation of the feed and effluent densities, i.e.  $H_{2,\beta} = f(d_{154,feed}, d_{154,eff})$ . This correla-  
204 tion is based on the n-d-m method (ASTM D-3238 [34]) is used.

205 Furthermore, three H<sub>2</sub> molecules are added for each full hydrogenation of an aromatic ring:  $H_{2,A} = 3 * (C_{A,feed} - C_{A,eff})$ .  
206 Measurements of the total amount of aromatic carbon atoms in the feed are available, and the extent of the hydro-  
207 dearomatisation reaction is estimated by a dedicated model not detailed here. The hydrogen added by the hydrodenitro-  
208 genation and hydrodesulfurization reactions is also taken into account.

### 209 3.4 Inhibition Terms

210 Zeolite catalysts are known to be inhibited by the presence of NH<sub>3</sub> gas[6]. An inhibition term ( $I_N$ ), based on the nitro-  
211 gen content in the feed of R1 ( $N_{R1}$ ) was therefore introduced in the model. The nitrogen in the feed of R1 is mostly trans-  
212 formed to NH<sub>3</sub>, which is carried over to R2. The inhibition term is therefore derived from an estimation of the partial  
213 pressure of NH<sub>3</sub> gas in the reactor, given in equation (9).

$$\frac{1}{ppNH_3} \propto \left( \frac{H_2 H_C}{P_{tot} N_{R1}} \right) \quad (9)$$

214 The residual nitrogen content in the feed of R2 ( $N_{R2}$ ) does also exhibit an inhibition effect on the zeolite catalyst. The  
215 nitrogen containing organic compounds adsorb on the acidic sites of the catalyst. These sites are therefore no longer  
216 available to perform hydrocracking reactions, until the nitrogen has been converted into NH<sub>3</sub> gas. The nitrogen contain-  
217 ing compounds remaining after a hydrotreatment step are generally very difficult to break down. The complete inhibition  
218 term used in this model is given in equation (10). A total of four tuning parameters allow the adjustment of this term to  
219 experimental data.

$$I_N = \left[ \frac{1}{(1 + \alpha_{NR2} N_{R2}^{\beta_{NR2}})} \right] \left[ \frac{1}{1 + \alpha_{NR1} \left( \frac{H_2 H_C}{P_{tot} N_{R1}} \right)^{\beta_{NR1}}} \right] \quad (10)$$

220 With:

$H_2 H_C$	Volumetric ratio of H <sub>2</sub> to hydrocarbon feed (in std L/L )
$P_{tot}$	Total pressure in R <sub>2</sub> (in bar)
$N_{R1}$	Organic nitrogen in feed of R <sub>1</sub> (in ppm)
$\alpha_{NR2}, \beta_{NR2}$	Model parameters
$N_{R2}$	Organic nitrogen in feed of R <sub>2</sub> (in ppm)
$\alpha_{NR2}, \beta_{NR2}$	Model parameters

### 221 3.5 Generation of Hydrocarbon Gas

222 The generation of hydrocarbons smaller than C<sub>5</sub> is treated separately in this model. It has been observed that the pro-  
 223 cess of generating these light gases is rather different and cannot be modeled by the same continuous yield distribution  
 224 used for the simulation of the cracking of heavier hydrocarbons. A separate term,  $g(\theta, GAS)$ , was therefore introduced in  
 225 the yield distribution.

$$g(\theta, GAS) = \alpha_{gas} \theta^{\beta_{gas}} e^{-\theta} \quad (11)$$

226 This term, shown in equation (11), uses a separate gamma function to estimate the total yield of C<sub>1</sub>-C<sub>4</sub> gas by cracking of  
 227 a hydrocarbon with TBP  $\theta$ . The additional model parameters ( $\alpha_{gas}$  and  $\beta_{gas}$ ) give further flexibility to the model.

228 The redistribution between C<sub>3</sub> and C<sub>4</sub> gasses are calculated using a dedicated correlation, which has been fitted sepa-  
 229 rately using a separate calibration database. Zeolite catalysts, such as the one used in this study, generate negligible  
 230 amounts of C<sub>1</sub> and C<sub>2</sub> gas. This is because the  $\beta$ -scission reaction mechanism cannot crack a hydrocarbon chain at the  
 231 ends.

### 232 4. Parameter Identification

233 The continuous lumping model presented in section 2.1 contains 12 tuning parameters. These parameters were identi-  
 234 fied using the calibration database presented in section 3.3. An objective function for a set of parameters ( $\beta$ ) was con-  
 235 structed, defined in equation (9), from the square difference between the experimental measurements ( $y$ ) and the simula-  
 236 tion results  $f(x, \beta)$ . Weights ( $w$ ) were applied different components of the objective function.

$$J = \frac{1}{2} \sum (y - f(x, \beta))^2 w (y - f(x, \beta)) \quad (12)$$

237 With:

$J$	Objective function
$y$	Experimental observations (vector)
$f(x, \beta)$	Organic nitrogen in feed of R <sub>1</sub> (in ppm)
$x$	Model inputs (vector)
$\beta$	Model parameters
$w$	Weights (diagonal matrix)

238

239 The yield structure (standard cuts & gasses C<sub>1</sub>-C<sub>4</sub>), the SIMDIS, and the total yield (100% + conso H<sub>2</sub>), as well as the  
240 SIMDIS (9 points), were used in the objective function, according to following weights ( $w$ ):

241	• Naphtha (< 150°C cut)	3
242	• Kerosene (150-250°C cut)	6
243	• Gasoil (250-370°C cut)	6
244	• Middle distillates (150-370°C cut)	10
245	• Residue (> 370°C cut)	10
246	• SIMDIS (10 - 90%)	0.01
247	• Gas yield (C <sub>1</sub> -C <sub>4</sub> )	10
248	• Total yield	1

249 It is important to note that the error in SIMDIS is expressed in terms of °C, while the other errors are expressed in terms  
250 of percentages. The former are an order of magnitude higher than the latter for a comparable fit of the model. A low  
251 weight was therefore chosen in order to obtain the same order of magnitude for all observables.

252 The DN<sub>2</sub>FB FORTRAN optimization routine, part of the PORT library (Bell Labs) was used for parameter identification  
253 [35]. This routine uses a Levenberg-Marquardt least squares algorithm to find the gradients of the objective function. The  
254 target function is highly non-linear. The optimized set of parameters was found to be highly dependent on the initial  
255 parameters, which implies convergence to local minima, rather than global ones in some cases. Optimizations were there-  
256 fore performed for a set of 96 randomly chosen initial parameters. Optimizations were performed on the high-  
257 performance cluster at IFP Energies Nouvelles, Solaize, France. The parameters of the case which converged to the lowest  
258 value of the objective function was retained.

259 This procedure does not guarantee convergence to the global minimum, it does, however, at the very least provide a  
260 good local minimum. The use of more advanced, global algorithms (i.e. genetic / global response surface algorithms) is far

261 more complex and time consuming than the gradient-based algorithm used in this study. This might be justified in a pure  
262 academic research context. The approach used in this study is better suited for practical applications, where a the model  
263 parameters for a new catalyst needs to be identified rapidly. The comparison of different optimization algorithms is per-  
264 formed at IPFEN and is the object of separate bodies of work.

## 265 5. Model Validation

266 The objective of the construction of a continuous lumping model for a hydrocracking process is the accurate estimation  
267 of yield structure and simulated distillation for a range of operating conditions. Estimation of the yield structure, in terms  
268 of standard cuts, is necessary in order to perform process design and optimization. It is common to design a hydrocrack-  
269 ing process in order to maximize the conversion of the residue cut ( $X_{370+}$ ) and the yield of the middle distillates (150 -  
270 250°C cut). The production of hydrocarbon gases (C1-C4) is generally undesirable [5].

271 The temperature of an industrial hydrocracking reactor is often adjusted to give a desired conversion ( $X_{370+}$ ). The rela-  
272 tionship between  $X_{370+}$  and yield structure is therefore of particular interest. For a given feed and catalyst, this relationship  
273 is relatively independent of reactor temperature. Simulations are run in two different modes:

- 274 1) iso-T: the real (measured) reactor temperature is used;
- 275 2) iso-RS: the temperature is adjusted such that the simulated residue content equals the experimental meas-  
276 ured value.

277 Good estimation of the SIMDIS of the effluent is necessary in order to calculate a number of product qualities for the  
278 individual cuts (e.g. d154, octane number, viscosity index, cetane index). This is done by dedicated correlations, based on  
279 the modeled SIMDIS.

280 Parity graphs, showing the agreement of simulation results and experimental measurements have been constructed for  
281 iso-T and iso-RS modes.

### 282 5.1 Iso-T mode

283 The results for residue conversion ( $X_{370+}$ ) and middle distillate yield in iso-T mode are shown in Figures 8 and 9.

284 The residue conversion is well predicted for the entire range, i.e. 15 to 100%. Some data points, particularly for the vali-  
285 dation database and/or for very high  $X_{370+}$ , tend to be somewhat under-predicted. The middle distillate yield (150-370°C) is  
286 very well predicted in iso-T mode. All points, with the exception of one point in the validation database, fall within an  
287 error band of  $\pm 5$  %. A summary of the mean absolute errors for a number of indicators is shown in Table 1.

288 The mean absolute errors for  $X_{370+}$  and yield structure for both, the calibration and validation database are very good for  
289 experimental runs with  $X_{370+} < 90\%$ . The errors are slightly higher but remain acceptable for the validation points. The  
290 points with very high residue conversion are less well predicted by the model. It is, however, important to note that in-  
291 dustrial hydrocracking units rarely operate at conversions higher than 90%. These points are therefore of somewhat lim-  
292 ited interest.

293 The possible reasons for this behavior are that the calibration database contained only two data points with  $X_{370+} > 90\%$ .  
294 The shape of the reactivity function in this region is therefore not sufficiently sensitized. The other reason is related to the  
295 fact that the SIMDIS becomes very steep around 370°C. This amplifies the error of residue ( $> 370^\circ\text{C}$  cut) yield, i.e. the  
296 point at which the SIMDIS and intersects the 370°C line. The mean absolute errors of hydrogen consumption and total  
297 yield show that the model ensures mass conservation and predicts the correct mass flowrates.

## 298 5.2 Iso-RS mode

299 A more detailed analysis is provided for the simulation results in iso-T mode. The simulation results for residue ( $>370^\circ\text{C}$   
300 cut) yield and thus  $X_{370+}$ , are fitted to experimental measurements in this mode. The yield structure of the model is ex-  
301 pected to improve with respect to iso-T mode. Figure 10 shows the middle distillate (150-370°C cut) yield. Kerosene (150-  
302 250°C cut) and gasoil (250-370°C cut), which make up the middle distillate are shown in Figures 11 and 12 respectively.

303 The middle distillate (150-370°C cut) yield is better predicted than in iso-T mode for points with  $X_{370+} < 90\%$ . The major-  
304 ity of points fall within the  $\pm 2\%$  error band. The high conversion points, on the other hand, are less well predicted in iso-  
305 RS mode than in iso-T mode. The parity graphs for the gasoil and kerosene yields show that the error in middle distillate  
306 comes mainly from the 250-370°C cut. Kerosene (150-250°C cut) yield is well predicted, even for elevated residue conver-  
307 sion. The gasoil (250-370°C cut) yield is poorly predicted for experimental runs with  $X_{370+} > 90\%$ , even though most points  
308 fall within a very narrow range ( $\sim 20\text{-}25\%$ ).

309 The parity graph for total hydrocarbon gas (C<sub>1</sub>-C<sub>4</sub>) shows that the continuous lumping model provides very good simu-  
310 lation results, even for high conversion ( $X_{370+} > 90\%$ ). Only three points of the validation database fall outside the error  
311 band of  $\pm 1\%$ . A summary of the mean absolute errors for a number of indicators is shown in Table 2.

312 The  $\Delta T$  values reported in Table 2 correspond to the mean temperature difference that had to be applied in order to ob-  
313 tain the desired  $X_{370+}$ . As in iso-T mode, the results for the validation database are slightly degraded with respect to the  
314 results obtained for the calibration points. A  $\Delta T$  of 2.0°C and an error of the yield structure of slightly more than 1% are  
315 well within the accuracy that can be expected from a hydrocracking model.



316 **6. Statistical Analysis of Model Parameters**

317 Statistics were calculated by an in-house code to quantify the relative importance and correlations between the parame-  
 318 ters. Standard non-linear optimization routines, such as DNzFB, attempt to determine the optimal set of parameters for  
 319 the best local minimum of the least-squares objective function. This implies a zero gradient hat around the optimal set of  
 320 parameters  $\beta_0$ :

$$Grad(J)(x, \beta_0) = 0 \quad (13)$$

321 The Taylor expansion of the objective function ( $J$ ), around the optimal parameters ( $\beta_0$ ), given the Hessian ( $H$ ) gives:

$$J(x, \beta) = J(x, \beta_0) + Grad(J)(x, \beta_0)(\beta - \beta_0) + \frac{1}{2}(\beta - \beta_0)'H(\beta - \beta_0) \quad (14)$$

$$J(x, \beta) = J(x, \beta_0) + \frac{1}{2}(\beta - \beta_0)'H(\beta - \beta_0) \quad (15)$$

322 The Eigenvector ( $v$ ), with the associated Eigenvalue ( $\mu$ ) of the Hessian ( $H$ ) is defined as:

$$\exists \mu > 0 \text{ such that } Hv = \mu v \quad (16)$$

323 A perturbation of  $\beta$  in the direction of the Eigenvector ( $v$ ) gives then, by definition:

$$\beta = \beta_0 + \alpha v \quad (17)$$

$$J(x, \beta) = J(x, \beta_0) + \frac{1}{2}\alpha v' H \alpha v \quad (18)$$

$$J(x, \beta) = J(x, \beta_0) + \frac{1}{2}\mu \alpha^2 ||v||^2 \quad (19)$$

324 An analysis of the components of the Eigenvector and the magnitude of the associated eigenvalues allows the relative  
 325 impact of variations of the individual parameters on the target function to be quantified. A small eigenvalue implies a  
 326 small impact of a variation of the parameters in the direction of the associated Eigenvector; inversely, a large eigenvalue  
 327 implies a large impact of a perturbation of the parameters in the direction of the associated eigenvector.

328 The Eigenvectors with their associated Eigenvalues are shown in Table 1. The dominant parameter in the first five Ei-  
 329 genvectors are highlighted to show the parameter with the largest impact on the objective function. This shows that the  
 330 model is very sensitive to the exponents of the nitrogen inhibition term ( $\beta_{NR_1}$  and  $\beta_{NR_2}$  in equation 8). The parameters of  
 331 the reactivity function (equation 4), the activation energy ( $E_a$ ), and the yield distribution (Equation 7) also have a large

332 influence on the model behavior. The parameters of the gas distribution (equation 9) have the least influence on the ob-  
333 jective function.

334 The correlation between the individual parameters can be determined from the symmetry in the Eigenvectors. This is  
335 shown in Table 4, higher values strong correlations. This table shows that the pre-exponential factor ( $k_0$ ) is strongly corre-  
336 lated with the inhibition term for NR<sub>1</sub>. The two parameters in the NR<sub>2</sub> inhibition term ( $\alpha_{NR_2}$  and  $\beta_{NR_2}$ ) are strongly corre-  
337 lated. The same can be said regarding the parameters governing the yield distribution for the gasses (Equation 11).

## 338 7. Conclusions

339 A continuous lumping model was successfully applied to hydrocracking of VGO feedstock on zeolite catalysts. The sec-  
340 ond reactor in a two-stage hydrocracking process was simulated. The model contains inhibition terms for NH<sub>3</sub> carried  
341 over from the pretreatment reactor (R<sub>1</sub>), as well as the residual organic nitrogen in the feed of the hydrocracking reactor  
342 (R<sub>2</sub>). A gamma function was used for the continuous reactivity function and a beta distribution was used for the yield  
343 distribution.

344 The 12 model parameters were identified using a calibration database with 52 data points. Parameter identification was  
345 performed using 96 sets of randomized initial parameters. The model was then used to simulate a validation database  
346 with 22 additional data points. Good simulation results, in terms of  $X_{370+}$  and yield structure were obtained. The model  
347 performed less reliably in the case of high conversion ( $X_{370+} > 90\%$ ).

348 A statistical parameters analysis, based on the Eigenvectors of the Hessian around the optimum was presented. This al-  
349 lowed the parameters with the largest impact on the objective function to be identified. An analysis of the correlation  
350 between the parameters was also presented. The eigenvector analysis was used to show that the nitrogen inhibition terms  
351 have (NR<sub>1</sub> and NR<sub>2</sub>) have a dominating effect on the target function. This makes it clear that the inclusion of these terms  
352 is absolutely necessary to correctly simulate hydrocracking of feeds with different nitrogen content and different levels of  
353 pre-treatment. Furthermore, a strong correlation between the nitrogen (NR<sub>1</sub>) inhibit terms and the pre-exponential factor  
354 has been shown.

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