MODELING OF HYDROTREATING PROCESSES VIA MOLECULAR FEED RECONSTRUCTION AND MOLECULE-BASED MONTE CARLO KINETICS

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Introduction

Hydrotreating (HDT) is one of the most important petroleum refining processes. The process consists of removing impurities such as sulfur, nitrogen and metals and reducing the aromatic content from petroleum fractions under a hydrogen pressure in the presence of a solid catalyst [1]. The HDT process can be used to enhance the quality of refined products so as to reach environmental constraints and commercial specifications as for kerosenes and gas oils, but also to pretreat feedstocks to other processing units such as naphtha cuts and vacuum gas oils.

To accurately predict process performances, reliable kinetic models are needed. Classic HDT kinetic models are based on a lumping strategy, in which molecular components are grouped into several chemical families, according to their global properties (boiling point, solubility, etc.). Hence, the actual molecular information is hidden due to the multicomponent nature of each lump. With environmental restrictions becoming more stringent, kinetic models have to be able to predict molecular properties of the products, a requirement that can not be achieved by using a lumped modeling strategy. Hence, more detailed kinetic models that contain molecule-based reaction pathways need to be developed. However, developing molecule-based kinetic models for complex petroleum feedstocks is intricate, not only due to the large number of chemical species, reactions and associated rate constants, but also due to difficulties arising in the characterization of these complex mixtures.

The present work focuses on the development of a novel two-step kinetic modeling strategy that retains the molecular detail throughout the method. In the proposed approach, the lack of molecular detail of the petroleum fractions is overcome by using a carefully selected synthetic mixture of representative molecules which has properties close to the available feedstock analyses. This mixture of molecules is generated in the first step of the methodology via a molecular reconstruction method. In the second step, a method called “kinetic Monte Carlo” (kMC) is utilized to simulate the reactions of this mixture of molecules. This method is based on a Markovian process, which transforms the molecule, event by event, by means of probability considerations. In this way, the reaction network is generated “on-the-fly” thereby reducing the size of the reaction network to be managed along the simulations.

The methodology has been applied to hydrotreating of two Light Cycle Oil (LCO) gas oils and the predicted effluents were favorably compared to the experimental yield pattern.

Composition modeling of the process feedstock

A representative set of molecules is generated using a molecular reconstruction algorithm, termed SR-REM [2,3]. This algorithm couples two methods, stochastic reconstruction (SR) [4,5] and reconstruction by entropy maximization (REM) [6]. The SR method is applied to generate an initial equimolar set of molecules that are typical for a given type of petroleum fraction. The REM method adjusts the molar fractions of the molecules to fine-tune the mixture properties. During previous works,
the SR-REM algorithm was applied to gas oil fractions \[2,7\], to vacuum gas oils \[8,9\], and to vacuum residues \[3,10,11\]. In the present work, the reconstruction of two LCO gas oil will be illustrated.

**Stochastic reconstruction (SR) method**

The idea behind the SR method is to transform the available analytical information into probability distribution functions (PDF) of molecular structural attributes (e.g. type of molecule, number of cores, number of aromatic rings, number of side chains, etc.). The PDFs can then be sampled to generate an equimolar set of molecules that has properties close to those of the process feedstock. The transformation of the analytical information into the PDF of the molecular attributes is carried out via an iterative procedure as shown in Figure 1.

![Building diagram](attachment://building_diagram.png)

**Figure 1.** Flow diagram of the stochastic reconstruction method.

First, the appropriate molecular attributes are chosen from the available analytical information (elemental analysis, \(^{13}\)C NMR, GC–MS, etc.) of the feedstock and from expert knowledge. A PDF is selected to represent each molecular attribute. The PDFs employed may either be discrete, such as histograms, or continuous, such as normal, gamma, or exponential distribution functions. Once appropriate PDFs are selected for each molecular attribute, they are sampled via a Monte Carlo procedure to determine the functional and structural attributes of a first molecule. The sequence of the PDF sampling steps is defined by a building diagram. The molecular attributes are randomly assembled, yet respecting chemical rules. These rules avoid the creation of impossible and improbable molecules on chemical, thermodynamic or probabilistic grounds. The construction of a molecule is repeated \(N\) times so as to obtain a synthetic mixture of \(N\) molecules. The pure component properties of each molecule are calculated, either directly, by inspection of the structure, or numerically, by group contribution methods or correlations \[2,3\]. The mixture properties are calculated from the pure component properties through linear mixing rules and compared to the available analyses by means of an objective function. The value of this objective function is then minimized via a genetic algorithm that iteratively modifies the parameters of the PDFs of the structural attributes. The iteration loop is repeated until the molecular representation accurately matches the properties of the process feedstock.

**Reconstruction by Entropy Maximization (REM) method**

The Reconstruction by Entropy Maximization (REM) method aims at adjusting the molar
fractions of a predefined set of molecules in order to obtain a mixture whose properties are closely aligned to those of the petroleum fraction [2,6]. This fine-tuning is performed by maximizing an information entropy criterion \( E(x_i) \) that is based on Shannon's information theory [12] and given by:

\[
E(x_i) = -\sum_{i=1}^{N} x_i \ln(x_i)
\]

where \( x_i \) represents the molar fraction of molecule \( i \) and \( N \) is the number of molecules present in the predefined set of molecules. This criterion ensures that in the absence of analytical information, no molecule is preferred, resulting in a uniform distribution of the molar fractions of the molecules. With constraints (analytical data), the entropy maximization distorts the distribution of molecules so as to achieve a correspondence between the properties of the mixture and the analytical data. For a more detailed description of the REM used in the present work, the reader is referred to previous work [2,6].

**Application to LCO gas oils**

LCO gas oils are gas oil fractions that are obtained from a catalytic cracking unit and contain paraffins, naphthenes, olefins and aromatics [2,13]. Sulfur and nitrogen species are also present, predominantly in heterocyclic structures, such as benzothiophenes or indoles [14,15]. The boiling point of the molecules ranges from 150°C to 350°C at atmospheric pressure, which corresponds to molecules with carbon numbers between \( C_{11} \) and \( C_{25} \) [2].

In the present work, LCO gas oils are described by 8 structural attributes which are shown in Table 1. Each molecule is initially defined according to the type of molecule, which may either be saturated (type 0) or aromatic (type 1). For saturated molecules, distribution 3 is sampled to determine the number of cyclohexane rings in the core. When the number of cyclohexane rings is equal to zero, the molecule is a paraffin and distribution 8 is sampled to determine its length. In the other case, the number and the length of the alkyl side chains of the naphthene molecules are determined by sampling distributions 6 and 7, respectively. For aromatic molecules, the number of benzene rings, cyclohexane rings and thiophene rings are selected through distributions 2, 3 and 4. Distributions 5 and 7 are then sampled to define the number and the length of the alkyl chains. For a more detailed description of the structural attributes, building diagram, property calculations and parameter optimization used in this work, the reader is referred to de Oliveira et al.[7,16].

<table>
<thead>
<tr>
<th>Structural attribute</th>
<th>Values</th>
<th>Distribution</th>
<th>Number of parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Type of molecule*</td>
<td>0, 1</td>
<td>Histogram</td>
<td>1</td>
</tr>
<tr>
<td>2. Number of benzenes rings</td>
<td>1,..., 4</td>
<td>Gamma</td>
<td>2</td>
</tr>
<tr>
<td>3. Number of cyclohexane rings</td>
<td>0,..., 4</td>
<td>Gamma</td>
<td>2</td>
</tr>
<tr>
<td>4. Number of thiophene rings</td>
<td>0, 1</td>
<td>Histogram</td>
<td>1</td>
</tr>
<tr>
<td>5. Substitution with alkyl chains (Aromatics)**</td>
<td>0, 1</td>
<td>Histogram</td>
<td>1</td>
</tr>
<tr>
<td>6. Substitution with alkyl chains (Saturates)**</td>
<td>0, 1</td>
<td>Histogram</td>
<td>1</td>
</tr>
<tr>
<td>7. Type of alkyl chain***</td>
<td>0, 1, 2</td>
<td>Histogram</td>
<td>2</td>
</tr>
<tr>
<td>8. Length of the paraffins</td>
<td>&gt;0</td>
<td>Gamma</td>
<td>2</td>
</tr>
</tbody>
</table>

* Type of molecule: 0 – saturated; 1 – aromatic
** Substitution with alkyl chains : 0 – no; 1 – yes
*** Type of alkyl chain : 0 – methyl, 1 – ethyl, 2 – propyl

The LCO gas oils were represented by 5,000 molecules in order to ensure an optimal balance.
between the required CPU time and the accuracy of the representation. Elemental analyses (carbon, hydrogen and sulfur), $^{13}$C NMR, mass spectrometry and simulated distillation were used as input to the SR-REM algorithm. All experimental data were obtained at IFP Energies nouvelles. The comparison between analytical and calculated properties of the LCO gas oil is shown in Table 2 and Figure 2.

Table 2. Comparison between experimental and calculated properties for the LCO gas oils.

<table>
<thead>
<tr>
<th></th>
<th>LCO I</th>
<th>LCO II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Analysis</td>
<td>Experimental</td>
<td>Set of molecules</td>
</tr>
<tr>
<td>Carbon wt.%</td>
<td>88.1</td>
<td>87.9</td>
</tr>
<tr>
<td>Hydrogen wt.%</td>
<td>10.4</td>
<td>10.6</td>
</tr>
<tr>
<td>Sulfur wt.%</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Aromatic CH at.%</td>
<td>22.3</td>
<td>22.2</td>
</tr>
<tr>
<td>Fused aromatic C at.%</td>
<td>7.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Substituted aromatic C at.%</td>
<td>13.3</td>
<td>13.2</td>
</tr>
<tr>
<td>Saturated CH$_2$ at.%</td>
<td>16.7</td>
<td>16.6</td>
</tr>
<tr>
<td>Saturated CH$_2$ at.%</td>
<td>32.0</td>
<td>31.9</td>
</tr>
<tr>
<td>Saturated CH at.%</td>
<td>7.7</td>
<td>7.6</td>
</tr>
<tr>
<td>Saturated C at.%</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Mass Spectrometry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n+2}$ wt.%</td>
<td>13.1</td>
<td>13.1</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{20}$ wt.%</td>
<td>9.9</td>
<td>9.9</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-2-4}$ wt.%</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-6}$ wt.%</td>
<td>7.1</td>
<td>7.2</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-8}$ wt.%</td>
<td>7.0</td>
<td>7.1</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-10}$ wt.%</td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-12}$ wt.%</td>
<td>16.7</td>
<td>16.7</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-14}$ wt.%</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-16}$ wt.%</td>
<td>6.9</td>
<td>6.9</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-18}$ wt.%</td>
<td>7.0</td>
<td>6.9</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{20}$ and more wt.%</td>
<td>4.6</td>
<td>4.5</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-10S}$ wt.%</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>C$<em>{n}$H$</em>{2n-16S}$ wt.%</td>
<td>6.9</td>
<td>6.9</td>
</tr>
</tbody>
</table>

For the two LCO gas oils, the properties of the synthetic mixtures of molecules are in good agreement with most of the analytical data. The elemental analysis and mass spectrometry are well represented. Some differences are, however, observed in the $^{13}$C NMR and partial simulated distillation curve. For the $^{13}$C NMR, the deviations are caused by the inconsistencies between the analyses, especially with the mass spectrometry and the $^{13}$C NMR. For the simulated distillation, the curve is calculated assuming that the molecules are perfectly separated by increasing adjusted boiling points, which is not strictly true, specially in the region near the initial and final boiling points [2]. Despite some bias, the results are in good agreement. The sets of generated molecules can be used as a correct molecular representation of the LCO gas oils to be used as an input for the hydrotreating kinetic model.
Kinetic modeling of the process reactions

The second step of the strategy simulates the effect of process reactions on the set of molecules generated in the previous step. To do this, the classic kinetic Monte Carlo (kMC) algorithm proposed by Gillespie [17], termed Stochastic Simulation Algorithm (SSA), was applied. In this work, LCO gas oil hydrotreating was simulated by applying its main reactions to the set of molecules via the SSA.

General description of the reaction simulation algorithm

The SSA is a numerical procedure to determine the temporal trajectories of the molecular population in a probabilistic way. The various steps of the SSA used in this work are illustrated in Figure 3.

The first step of the algorithm is the “molecular discretization” of the feedstock that was previously generated by molecular reconstruction. The process feedstock obtained by the SR-REM algorithm is represented by a set of molecules and their mole fractions. However, the kMC method does not track the mole fractions of the molecules, but the transformations of discrete molecules. Similarly to the quantitative approach proposed by Hudebine and Verstraete to create a representative database of molecules for gasoline fractions [6], this approach replicates the molecules according to their mole fractions in order to obtain a set of discrete molecules.

Once the molecular discretization step has been performed, all potential reactions are identified from the structure of each reactant molecule by means of reaction rules. The normalized probability of each reaction is determined based on the probability \( a_i \) that reaction \( v \) will occur in the reaction volume \( V \), divided by the sum of all probabilities for all possible reactions:

\[
P_v = \frac{a_v}{\sum_{w} a_w}
\]  

The probability for reaction \( v \) is defined as the product of the number of distinguishable combinations of the reactant molecules \( h_v \) and the rate parameter \( c_v \), as illustrated by the equation (3). For monomolecular reactions, the number of distinguishable combinations of the reactant molecules \( h_v \) equals 1.

\[
a_v = h_v \cdot c_v
\]
In the SSA, a first random number (RN\(_1\)) is drawn to determine the reaction time step (\(\Delta t\)) between the current time \(t\) and the time at which the next, yet undefined, reaction will occur. This reaction time step is calculated using equation (4), as proposed by Gillespie [17]:

\[
\Delta t = -\frac{\ln(RN_1)}{\sum \frac{1}{A_i}}
\]  

(4)

The cumulative probability distribution (\(D_R\)) at time \(t\) contains all reactions that can occur in the mixture at that reaction time. The probability of each reaction is given by their rate constant and the number of occurrences of this reaction. In Gillespie's SSA, this cumulative probability distribution \(D_R\) is then randomly sampled by means of a second random number (RN\(_2\)) in order to select the next reaction \(\mu\) that will be executed in the next reaction time step. The value of this random number selects the next reaction from the cumulative probability distribution \(D_R\), as shown in equation (5):

\[
D_R(\mu - 1) < RN_2 \leq D_R(\mu)
\]  

(5)

Once the reaction time step \(\Delta t\) has been determined and the reaction has been selected, the reaction system is updated by executing the selected reaction and incrementing the simulation time by \(\Delta t\). The simulation thus proceeds event-by-event until the final simulation time is reached. The molecule mixture at the end of the simulation now represents the effluent of the process.

**Figure 3.** Schematic representation of the Stochastic Simulation Algorithm (SSA).

**Simulation of the hydrotreating of LCO gas oil**

The experiments were carried out in an isothermal fixed-bed up-flow reactor containing 200 ml of a sulfided commercial NiMo/Al\(_2\)O\(_3\) catalyst [13,18]. The operating conditions were varied over a wide range: temperature was varied between 320°C and 390°C, total pressure ranged from 20 to 110 bar, while the range for LHSV was varied between 0.5 and 4 h\(^{-1}\).
LCO gas oil hydrotreating was simulated by accounting for the hydrogenation of aromatic rings, the dehydrogenation of saturated rings and the hydrodesulfurization (HDS) of thiophene rings. The reaction probabilities $a_ν$ for hydrogenation reactions are calculated from equation (6):

$$a_{\text{Hydro}} = c_{\text{Hydro}} P_{\text{Hydro}}$$  

where $c_{\text{Hydro}}$ is the stochastic rate parameter for hydrogenation, $P_{\text{Hydro}}$ is the hydrogen partial pressure, and $n_ν$ is the reaction stoichiometry with respect to hydrogen molecule. The stochastic rate parameter for hydrogenation is calculated using a Quantitative Structure / Reactivity Correlation (QS/RC) that was developed by de Oliveira [16] and given in equation (7):

$$\ln(c_{\text{Hydro}}) = -4.65 - 7.06 n_ν^{1.18} - 1.08 \frac{\Delta H^0_{\text{R}}}{R} + 0.616 N_{\text{AR}} + 0.330 N_{\text{SR}} - 2.80 N_{\text{TR}} \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)$$  

where $n_ν$ is the reaction stoichiometry with respect to hydrogen, $\Delta H^0_{\text{R}}$ is the heat of hydrogenation reaction at 25°C, $N_{\text{AR}}$ and is the number of aromatic (benzene) rings of the molecule, $N_{\text{SR}}$ is the number of saturated (cyclohexane) rings of the molecule, $N_{\text{TR}}$ is the number of thiophene rings fused to the aromatic ring, $E_a$ is the activation energy for hydrogenation, $R$ is the ideal gas constant, $T$ is the reaction temperature, and $T_{\text{ref}}$ is the reference temperature.

For the dehydrogenation reactions, the reaction probabilities $a_ν$ are given by the stochastic rate parameters $c_ν$ and calculated to be thermodynamically consistent with the hydrogenation reactions. This therefore leads to the following expression for the dehydrogenation reaction probability:

$$a_{\text{Dehydro}} = c_{\text{Dehydro}} = \frac{c_{\text{Hydro}}}{K_{\text{eq}}}$$  

where $c_{\text{Dehydro}}$ is the stochastic rate parameter for dehydrogenation, and $K_{\text{eq}}$ is the equilibrium constant. For the equilibrium constant $K_{\text{eq}}$, the Quantitative Structure / Reactivity Correlation (QS/RC) given in equation (9) has been developed by de Oliveira [7,16]:

$$\ln(K_{\text{eq}}) = 2.952 - 13.215 n_ν + 5.196 \cdot 10^{-3} \frac{\Delta H^0_{\text{R}}}{R} - 0.784 N_{\text{SR}} - \frac{\Delta H^0_{\text{R}}}{R} \frac{1}{T} - \frac{1}{T_{\text{ref}}}$$  

where $n_ν$ is the reaction stoichiometry in respect to hydrogen molecule, $\Delta H^0_{\text{R}}$ is the heat of hydrogenation reaction at 25°C, $N_{\text{SR}}$ is the number of saturated rings (cyclohexane) of the molecule, $R$ is the ideal gas constant, $T$ is the temperature of the system and $T_{\text{ref}}$ is the reference temperature.

The HDS reactions are considered to be first order or pseudo-first order reactions with respect to the reacting molecule. For each molecule, the reaction probability $a_ν$ is obtained using equation (10):

$$a_{\text{HDS}} = c_{\text{HDS}}(T_{\text{ref}}) \exp \left( -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right)$$  

where $c_ν$ is the stochastic rate constant of the reaction type $ν$ at the reaction temperature, $c_ν(T_{\text{ref}})$ is the stochastic rate constant of the reaction type $ν$ at the reference temperature $T_{\text{ref}}$, $E_a$ is the activation energy, $R$ is the ideal gas constant, $T$ is the temperature of the system and $T_{\text{ref}}$ is the reference temperature.

It is well-known that the HDS reactions can either follow a hydrogenolysis pathway or a hydrogenation pathway [19,20]. The HDS reactions of the hydrogenolysis pathway are classified into five families according to the molecular structure of the reacting sulfur compound, as described in Table 3. For hydrogenation pathway, saturation of the benzene rings fused to the thiophene ring is assumed to follow a classical hydrogenation reaction and its rate constant is estimated by equation (6). The thiophene saturation and subsequent removal of the sulfur atom is assumed to occur in a single step and its rate parameter is equal to that of the hydrogenolysis of thiophene or benzothiophene.
The rate parameters of the various reactions were fitted to the experimental data obtained during hydrotreating of the LCO I (cf. Figure 4) and their values are presented in Table 3. To reduce the number of degrees of freedom, all activation energies were obtained from literature [18].

**Table 3.** Reaction families and their rate parameters, activation energies and reference temperature.

<table>
<thead>
<tr>
<th>Reactions families</th>
<th>$c_r$ (h$^{-1}$)</th>
<th>$E_a$ (J/mol)</th>
<th>$T_{ref}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenation / Dehydrogenation</td>
<td>Equations (6)-(9)</td>
<td>50,942</td>
<td>320</td>
</tr>
<tr>
<td>Hydrodesulfurization of heterocyclic compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogenolysis of thiophene and their derivatives</td>
<td>8.0 x10$^3$</td>
<td>50,000</td>
<td>320</td>
</tr>
<tr>
<td>Hydrogenolysis of BT and their derivatives</td>
<td>5.0 x10$^3$</td>
<td>70,000</td>
<td>320</td>
</tr>
<tr>
<td>Hydrogenolysis of DBT and their derivatives</td>
<td>8.0 x10$^3$</td>
<td>84,991</td>
<td>320</td>
</tr>
<tr>
<td>Hydrogenolysis of 4-alkyl-DBT and their derivatives</td>
<td>5.0 x10$^3$</td>
<td>113,340</td>
<td>320</td>
</tr>
<tr>
<td>Hydrogenolysis of 4,6-dialkyl-DBT and their derivatives</td>
<td>5.0 x10$^4$</td>
<td>120,416</td>
<td>320</td>
</tr>
</tbody>
</table>

The hydrotreating simulations are repeated 50 times and the mixture properties of the populations of molecules are averaged. The comparison between the predicted and experimental data of the LCO I and LCO II is shown in Figure 4 and Figure 5, respectively. For each figure, the left hand side graph (HDA) corresponds to the prediction of the saturated and aromatic compounds, which are grouped into four chemical families: saturates (SAT), monoaromatics (MONO), diaromatics (DI) and heavier aromatics (TRI+), while the temporal evolution of BTs and DBTs are presented in the right hand side graph (HDS). In these graphs, the lines represent the simulation results and the points correspond to the experimental data.

![HDA and HDS graphs](image.png)

**Figure 4.** Comparison between experimental and calculated values for the aromatic and sulfur families during hydrotreating of LCO I.

For both LCOs, the prediction of the hydrogenation of aromatics compounds is quite accurate, despite the fact that a slight deviation can be observed for the TRI+ family. This deviation may be caused by the exponent of the $n_9$ reaction index that was introduced in QS/RC for the hydrogenation rate constant (cf. equation (7)) [7]. However, the evolution of the aromatic compounds is generally better predicted with this exponent than without it.

For sulfur removal, a very good agreement is obtained between the simulated and experimental values in both cases. These results are even more remarkable considering the fact that the performances on the hydrotreating of LCO II (cf. Figure 5) were predicted using, without modification, rate
parameters that were adjusted to the experimental data for hydrotreating of LCO I (cf. Figure 4). Moreover, the molecular composition of LCO II is quite different from that of LCO I (cf. Table 2).

**Figure 5.** Comparison between experimental and calculated values for the aromatic and sulfur families during hydrotreating of LCO II.

**Conclusions**

A novel two-step kinetic modeling strategy for hydrotreating has been described and illustrated. In the first step, a set of molecules representing the process feedstock is generated using a molecular reconstruction algorithm. The second step consists in simulating the effect of the hydrotreating reactions on the generated set of molecules using a kinetic Monte Carlo method. In this work, the methodology was successfully applied to the hydrotreating of two Light Cycle Oil (LCO) gas oils. These results illustrate that the methodology is able to provide a good prediction of the hydrotreating behavior of complex feeds, even though the molecular composition of feeds are very different.

The proposed approach has several advantages. The complex feedstock is represented by means of a polydisperse synthetic mixture of molecules. This molecular representation is retained throughout the entire reactor simulation. Moreover, the simulation of the reactions can be performed without a pre-defined kinetic network. Indeed, in the SSA method, the kinetic network is generated "on-the-fly” as the reactions proceed.

**References**