"Développement d'une méthodologie de modélisation cinétique de procédés de raffinage traitant des charges lourdes"
("Development of a kinetic modeling approach for refining processes treating complex feedstocks")
PhD thesis of Luis Carlos PEREIRA DE OLIVEIRA

Summary

For refining processes that treat complex mixtures, such as heavy oil fractions, a better understanding of the chemical phenomena and their modelling constitutes a major obstacle for the development of more efficient and environmentally friendly technologies. The present PhD thesis focuses on the development of an innovative and original methodology for the kinetic modeling of heavy oil conversion processes. The methodology models both the feedstock composition and the process reactions at a molecular level.

The composition modeling consists in generating a set of molecules whose properties are close to those of the process feedstock analyses. This synthetic mixture of molecules is generated by a two-step molecular reconstruction algorithm. In its first step, an equimolar set of molecules is built by assembling structural blocks in a stochastic manner. In the second step, the mole fractions of the molecules are adjusted by maximizing an information entropy criterion. Once the composition of the feedstock is adequately represented, the conversion process is simulated by applying, event by event, its main reactions to the set of molecules by means of a kinetic Monte Carlo (kMC) method.

This methodology has been applied to two refining processes: The hydrotreating (HDT) of Light Cycle Oil (LCO) gas oils and the hydroconversion of vacuum residues (VR). For the HDT of LCO gas oils, the overall properties of the effluent are well predicted for various feedstocks and operating conditions. The methodology is also able to predict molecular properties of the effluent that are not accessible through traditional kinetic models. For the hydroconversion of VR fractions, which contain much more complex molecules than LCO gas oils, the conversion is well predicted and the overall product yields and product property predictions follow the correct trends with the operating conditions. Further work will focus on improving the accuracy of these predictions.

The importance of this work goes beyond the specific cases discussed in this thesis. The thesis shows that the stochastic approach is viable for systems of such complexity and their flexibility is an asset for the modelling of processes treating complex feedstocks.

Problem addressed

The need to convert crude oil residue into cleaner and more valuable liquid products is a major driver for the refining industry. The world demand for high-quality petroleum products such as gasoline and diesel is continually increasing, while the market demand for low value products such as fuel oil and residua based products is decreasing. Moreover, residues represents a significant portion of a barrel of crude oil (approximately 50 vol% for typical crude oils, and up to 85 vol% for heavy crudes).[1,2] At the same time, environmental regulations on petroleum products have forced stringent constraints upon the required product quality. Many of these constraints are phrased in terms of molecular or atomic composition of the feedstocks and process products. Therefore, the design and optimization of residue conversion processes require a better understanding of the chemistry occurring during the processing of these feedstocks.

Petroleum residue conversion processes, such as residue hydrocracking, residue fluid catalytic cracking (RFCC) or delayed coking, are, however, complex reaction systems. The chemistry of these processes is usually obscured by the heterogeneous, multicomponent character of the reacting mixture. Petroleum residue is an extremely complex mixture of hydrocarbons that contains several

thousands of different species. These chemical species are mainly composed of carbon and hydrogen, but also contain heteroatoms such as sulfur, nitrogen and oxygen [3]. Due to its complexity, no analytical technique is currently powerful enough to provide a molecular composition of a petroleum residue. This mixture is usually characterized by its overall properties, such elemental analysis, density, or boiling point distribution (distillation). In order to address the optimization and design concerns, an accurate and reliable reaction model is needed to better understand the molecular chemistry involved in conversion processes.

The present work focuses on the development of a general methodology for kinetic modelling of heavy oil refining processes using molecular-level techniques. This ambitious target was set out in order to circumvent existing limitations in the characterization of complex feedstocks and to account for the very large number of reactions that occur during the transformation of such complex feeds.

State of the art

Reaction models for optimizing conversion processes need to be increasingly more detailed, firstly to account for the extensive diversity of feedstocks and, secondly, to account for the increasingly stringent specifications on product quality. The development of reaction models is however a challenging task due to the complexity of petroleum residues, but also to the complex chemistry which governs the transformation of these feedstocks. Classic kinetic models for complex systems have been based on a lumping approach. This modeling approach consists in regrouping chemical compounds by similar global properties into groups, called "lumps". The lumps are then considered as homogeneous. Between the various lumps, a kinetic model is then developed, as if these lumps were actual chemical species. However, such models have several shortcomings. First of all, the lumping approach assumes that similar physical properties result in similar chemical reactivities and that the properties of these families do not change during the reaction, which is not necessarily true. Secondly, lumped models are not based on a molecular kinetic theory but are optimized directly from experimental data over a limited number of feedstocks and operating conditions. Thus, such models are reliable within a limited range of operating conditions and for some feedstocks. Thirdly, the number of model parameters (rate constants, activation energies, adsorption parameters) is proportional to the number of lumps. Hence, a high number of model parameters must be identified when modeling processes treating complex feedstocks. Finally, lumped models are not really able to determine the physicochemical properties of the mixture from the composition and the properties of their lumps. In practice, these models need to use correlations in order to provide an estimation of the desired properties, but such estimation methods are very empiric and limited.

The limitations of lumping models motivated the development of more fundamental kinetic models containing more detailed reaction pathways. According to the level of description detail of the reaction pathways, such models can be classified into two different approaches: mechanistic and molecular.

Mechanistic models are a more fundamental approach using detailed explicit description of the reaction pathways, including elementary steps, e.g. protonation, deprotonation, β-scission, isomerization, hydride abstraction, and both molecules and reaction intermediate species, such as the ions and radicals. Several mechanistic models have been developed and described in the literature for different applications, such as catalytic cracking [4–6], hydrocracking [7–9], hydrocarbon pyrolysis [10–12], catalytic reforming [13,14]. This approach requires few assumptions and the rate parameters are more fundamental in nature. However, this approach is not suitable for processes treating very complex mixtures, such as residue conversion processes. The number of compounds and the number of reactions (and consequently rate parameters) involved in petroleum processes increases exponentially with the number of carbon atoms of the species involved. The number of species quickly exceeds several thousands of molecules. Therefore, for complex feedstock, the reaction network turns out to be so large that, even when applying the network reduction techniques, it becomes difficult to manage along the simulations.

Molecular models are an intermediate approach between the mechanistic and lumping approaches that model a chemical system at molecular level without including the reaction intermediates species. The reactions are viewed as molecule-to-molecule transitions and each one is characterized by an overall kinetic constant. The effects of reaction intermediate species are included in the expression of rate laws by imposing some assumptions. Some molecular models have been developed to refining processes. Allen and Liguras [15,16] developed a molecular model for the vaccum gas oil (VGO) pyrolysis, Neurock [17,18] proposed to model the asphaltenes pyrolysis based on molecular Monte-Carlo techniques, and Quann and Jaffe [19,20] developed a model of the catalytic cracking using the SOL (structure oriented lumping) method. The molecular approach are also applied to gas oil hydrotreating processes [21].

The present short state of art illustrated that molecule-based kinetic modelling is more appropriate for modelling the conversion processes because the reaction model retains a molecular detail of the chemical systems, such mechanistic approach, by using a simplified reaction network. However, the molecular models expect a molecular description of the feedstocks which cannot be obtained via de analytical techniques for the complex feedstocks. This drawback can be overcome by creating a molecular representation of the feedstock through the reconstruction algorithms. This reconstruction algorithm aims to generate a set of molecules from available analytical information, model hypotheses and chemical knowledge. In the literature, several molecular reconstruction approaches have been described to represent complex feedstocks[16,19,20,22–24]. These reconstruction methods can be classified into two groups according to approach used to represent the molecular composition: deterministic modelling approach and stochastic modelling approach.[25]. For heavy oil fractions, where the analytical characterization is very limited, the stochastic modelling technique is the more suitable approach.

Key innovations, applications, implementations and results

The present PhD thesis focuses on the development of a general methodology for the kinetic modelling of heavy oil refining processes (cf. Figure 1). The proposed methodology comprises two mains steps : composition modelling and reaction modelling.
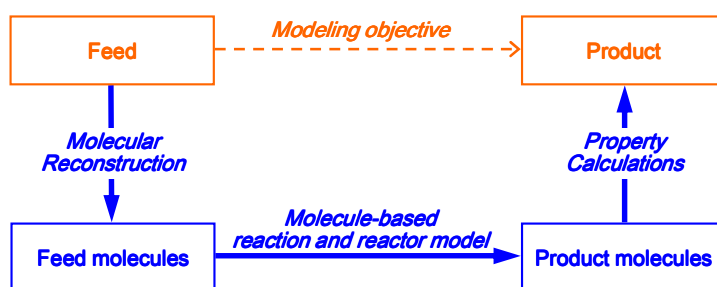

Figure 1. Schematic representation of the kinetic modeling methodology proposed in thePhD thesis.

In the first step, the feedstock composition is modeled by means of a set of molecules whose mixture properties are close to the process feedstock analyses. The set of molecules is generated using SR-REM molecular reconstruction algorithm [24,26]. This algorithm results from the coupling of two reconstruction methods: stochastic reconstruction (SR) [23] and reconstruction by entropy maximization (REM) [27]. The SR algorithm generates an equimolar set of molecules that are typical for a feedstock process. The molecules are generated by assembling structural blocks which are found by sampling a set of probability distribution functions (PDF) for molecular structural attributes (number of rings, chains length, number of chains). The transformation of the analytical information into PDFs of molecular attributes is carried out via an iterative procedure [26]. The REM algorithm consists to adjust the mole fractions of the molecules in order to achieve a close correspondence

between the mixture properties of the set of molecules and the process feedstocks analyses. The adjustment is performed by maximizing a Shannon entropy criterion based on the information theory developed by Shannon [28].

The SR-REM molecular reconstruction algorithm was initially developed by Hudebine for modelling LCO gas oils composition [24]. In the present thesis, the SR-REM algorithm was extended to vacuum residues (VR) by creating the PDF molecular structural attributes adapted for this petroleum cut. Moreover, two variants of this algorithm have been proposed to reconstruct the vacuum residues : direct RS-REM algorithm and indirect RS-REM algorithm. To validate these two variants, 8 VR fraction from different origins are successfully reconstructed[26]. Finally, a sensitivity analysis of the effect of the repeatability of the analyses on the results of the reconstruction, and the impact of reconstruction on the prediction of residue hydrotreating performance was also carried out.

In the second step of the methodology, a "Kinetic Monte Carlo" (kMC) method is utilized to simulate the effect of the process reactions occurring on the mixture of molecules generated in the composition modeling step. This method is based on a Markovian process, which track the transformation of a discrete population of molecules, event by event. Each event describes the transition from one state to another resulting from a chemical reaction. For each transition (or reaction), a probability function is associated, which depends on the molecules involved in the reaction and the rate constant. The kMC method does not need the exhaustive reaction network, but a list of reaction rules that describe the possible transformations for each molecule. In this way, the network can be generated "on-the-fly". Thus, the kMC method becomes better suited for the simulation of processes treating heavy fractions than the traditional method.

In the present thesis, an computer simulation code was created to simulate the transformation of the molecules in the refining processes. This simulation code is based on an KMC method , called "stochastic simulation algorithm" developed by Gillespie [29]. To simulate the refining process transformations, 7 reactions families are included in the simulation code: hydrogenation of aromatic rings, dehydrogenation of saturated rings, hydrodesulphurization of thiophene rings, hydrodesulphurization of sulfides, ring dealkylation, ring opening and paraffin cracking. Finally, the Quantitative Structure / Reactivity Correlation (QS/RC) are also developed for estimating the rate parameters of the hydrogenation reactions.

The proposed methodology was applied to two refining processes: The hydrotreating (HDT) of Light Cycle Oil (LCO) gas oils and the hydroconversion of vacuum residues (VR). The first case concerns the hydrotreating simulation of two LCO gas oils with different molecular characteristics [30]. 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 [31]. 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}.

The two LCO have been represented by a set of 5000 molecules which were generated from elemental composition (carbon, hydrogen, sulfur), ^{13}C NMR, mass spectrometry and simulated distillation. Hydrotreating reactions was modeled by applying the hydrogenation of aromatic rings, the dehydrogenation of saturated rings and the hydrodesulphurization (HDS) of thiophene rings. The evolution of the set of 5000 molecules was assessed by performing 50 stochastic simulations and averaging the properties of the mixture. The comparison between the predicted and experimental data of the LCO I and LCO II is shown in Figure 2 and Figure 3, respectively.

For both LCOs, a very good agreement is obtained between the simulated and experimental values for hydrogenation of aromatics compounds and sulfur removal. These results are even more remarkable considering the fact that the performances on the hydrotreating of LCO II (cf. Figure 3) were predicted using, without modification, rate parameters that were adjusted to the experimental data for hydrotreating of LCO I (cf. Figure 2). Moreover, the molecular composition of LCO II is quite different from that of LCO I, which can be seen by comparing the ratios BT/DBT and SAT/MONO at t =

0h. These results illustrate that the proposed molecule-based modeling approach is able to provide a good prediction of the refining process behavior for feeds having different molecular properties which remains problematic in the case of the lumping models.
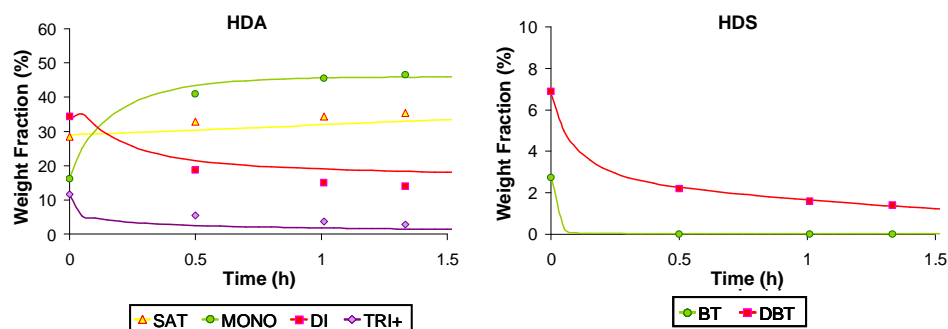

Figure 2. Comparison between experimental and calculated values for the hydrocarbon families (SAT – Saturates, MONO – Monoaromatics, DI – Diaromatics, TRI+ - Polyaromatics) and sulfur families (BT – Benzothiophenes, DBT – Dibenzothiophenes) during hydrotreating of LCO I.
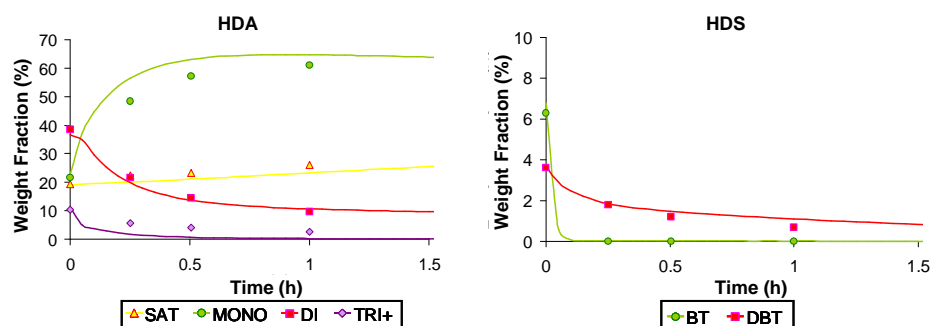

Figure 3. Comparison between experimental and calculated values for the hydrocarbon families (SAT – Saturates, MONO – Monoaromatics, DI – Diaromatics, TRI+ - Polyaromatics) and sulfur families (BT – Benzothiophenes, DBT – Dibenzothiophenes) during hydrotreating of LCO II.

The second application case is the hydroconversion of an Athabasca VR. The hydroconversion experiments were performed in a batch reactor using a 300 ml autoclave. Experiments have been carried out at 410°C and three different reaction times (1, 2, and 3 hours). The reactor was usually charged with 50 g of feedstock and 0.5 g of crushed industrial sulfided NiMo equilibrium catalyst, pressurized with hydrogen in excess and quickly (less than 15 minutes from 100 °C to 420 °C) heated to the reaction temperature. At the end of the reaction (after 1 to 3 hours), the reactor was quickly (less than 15 minutes from 420 °C to 100 °C) cooled down with an air vortex system.[32] The Athabasca VR composition was modeled through a set of 5000 molecules. The set of molecules were generated from elemental composition (carbon, hydrogen, sulfur, nitrogen, oxygen), ^{13}C NMR, average molecular weight, SARA analysis and partial simulated distillation using the direct SR-REM molecular reconstruction algorithm [33]. Despite of the fact that VR fractions contain more complex molecules than LCO gas oils, the SR-REM algorithm has generated an accurate molecular representation of Athabasca VR (cf. graphs of Figure 4 at t = 0).

The hydroconversion of VR were simulated by accounting for the dealkylation of rings, opening of rings without alkyl chains, hydrogenation of aromatic rings, dehydrogenation of saturated rings and hydrodesulphurization of thiophene rings and sulfides. The hydroconversion simulations were repeated 100 times and the mixture properties of the populations of molecules are averaged. The comparison between the predicted and experimental data for sulfur removal and product yields is illustrated in Figure 4.
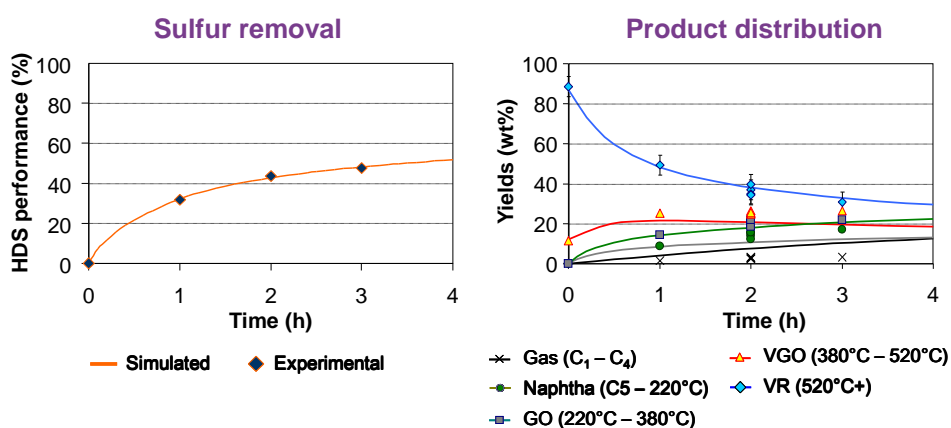
Figure 4. Comparison between experimental and estimated data for sulfur removal and product yields of Athabasca VR hydroconversion.

The left hand side graph of Figure 4 shows the sulfur removal performance, while the temporal evolution of the yields of the petroleum product fractions obtained from the VR conversion are illustrated on the right hand side. As shown in the graphs, the conversion of VR (blue line in right graph) and sulfur removal are well predicted. However, the results for petroleum product yields are less accurate. The proposed methodology is currently still being improved for the hydroconversion of VR, by including new ring opening reactions and by refining the feedstock representation with additional molecular information from the analyses of the process effluents.

As illustrated in LCO hydrotreating case, the proposed molecule-based kinetic modeling approach not only allows predicting the global information of the process, such as its yield structure and hydrotreating performances, but it also provides many molecular details throughout the reactor simulation. Indeed, one can easily "regroup" the molecules of the synthetic mixture so as to assess the evolution of the concentrations of various chemical families or molecular structural information, as illustrated in Figure 5 [34].
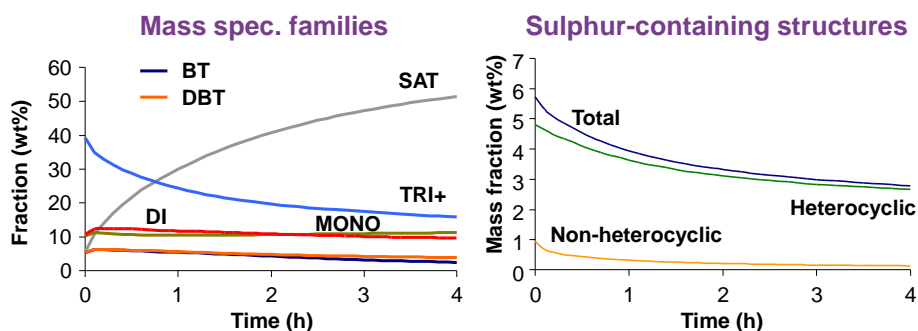

Figure 5. Average temporal evolution of mass spectrometry families and sulfur-containing structure for Athabasca VR hydroconversion.

The present PhD thesis is an important step towards a universal treatment of compositional and kinetic modeling of complex feedstocks using a molecular-level approach. It demonstrated that the molecule-based kinetic modelling approach is adapted to the overwhelming complexity of the complex multi-component feedstocks and allows to adequately represent the performance of industrial processes. Moreover, it was shown that the differences between the experimental results and the simulations allow to gain insight into the various molecular processes and to account for all relevant steps. The thesis shows that the stochastic approach is viable for systems of such complexity. It demonstrates that the stochastic methods correctly reproduce the known characteristics and predict non-measurable properties, even in cases with relatively limited analytical knowledge. This opens the way for applying stochastic methods, taking full advantage of their flexibility, to similar problems, which arise in pharmacy, biology and the environmental sciences.

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