

# Kinetics mechanism of asphaltenes liquid-phase pyrolysis

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## Abstract

The world energy demand is continuously increasing while the energy supply is still strongly related to fossil fuel, and likely to stay so in the near future. However, the availability of high-quality crude oil feedstocks is constantly depleting. Heavy Fuel Oils (HFOs) are expected to play a vital role in the future of the energy supply as fuels for power generation and marine shipping. This work presents the first step in the formulation of a kinetics model aimed to reconstruct the HFOs pyrolytic behavior as the weighted sum of their SARA (Saturates, Aromatics, Resins, Asphaltenes) fractions contribution.

In this work, details of the model to describe the asphaltenes pyrolysis is reported. The development of the model followed two main steps. The first one concerned the formulation of a suitable characterization framework being HFOs and asphaltenes complex mixtures made by thousands of different compounds. The characterization framework is based on the design of five pseudo components which are used to generate surrogate mixtures to mimic actual asphaltenes samples. The surrogate mixture is generated as the linear combination of pseudo components to reproduce the sample's elemental composition. The pseudo components structure was designed taking advantage of experimental information from literature and in-house experiments performed at King Abdullah University of Science and Technology (KAUST). The second step was the development of the pyrolysis kinetics scheme. The formulation of the kinetic model proceeded through chemistry-related considerations intending to reproduce the all-significant pyrolysis products. A reaction pathway is assigned to each pseudo component with the task to approximate the overall kinetics. Model parameters such as activation energy, pre-exponential factors, and stoichiometric coefficients of each reaction were tuned following a data fitting approach to match experimental evidence.

The model obtained is predictive and versatile being able to reproduce the pyrolytic behavior of different asphaltenes samples just knowing their elemental composition. The mechanism of asphaltenes represents a first step in the formulation of a comprehensive kinetics scheme for HFOs, which can be adopted for design, tuning, and optimization of combustion modeling processes.

### Keywords:

surrogate, HFOs, pseudo-components, pyrolysis, chemical kinetics modeling, Asphaltenes

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## 1. Introduction

The world energy demand is continuously increasing, propelled by population growth and developing economies. In recent, many investments have been made to improve the quality and the quantity of energy produced by renewables. Despite that, the energy market is still strongly related to fossil fuels, and continue to be so for the next few decade [1]. However, the availability of high-quality crude oil feedstock is constantly depleting. According to Demirbas et al. [2] more than 50% of the world oil reserves are in the form of restorable oil such as heavy oil, extra-heavy oil, oil sand, tar sands, and oil shale, and bitumen. Heavy Fuel Oils (HFOs) consist of liquid fuels that can be identified as the distillate or residual fraction of crude oil. The heavier the crude oil is, the higher the expected amount of residual is. Hence, it is reasonable to think that the energy market will become more reliant on HFOs in the future. HFOs are mainly used as fuel for industrial burners and marine transportation, but they can also be used as feed for a gasifier to produce syngas and hydrogen. Almost all the HFOs industrial applications involve liquid-phase pyrolysis. Many challenges have to be faced with finding cost-effective HFOs upgrade processes. HFOs are characterized by high viscosity, high pollutant release, and contaminants but the strongest challenge is physico-chemical complexity. HFOs are complex mixtures made by thousands of different species distribute in a wide boiling point range (25 °C to 800 °C) [3, 4]. Nowadays, a widely adopted characterization technique for HFOs is the SARA analysis. Following this technique, HFOs are divided into four fractions based on solubility and polarity: Asphaltenes, Resins, Aromatics, and Saturates. This work will be focused on Asphaltenes which are briefly described.

By definition, Asphaltenes are the fraction separated by precipitation in an n-alkane solvent, generally n-heptane [5]. Asphaltenes are the main critical fraction being responsible of many problems like viscosity increase, stabilize emulsion making distillation more complex, and reducing combustion efficiency being easily converted to particular matter [6]. Asphaltenes' chemical structure has been widely debated. The molecular weight was reported in the range of  $10^3$  to  $10^4$  g/mol. However, the measurements were not reliable due to the asphaltenes tendency to form aggregates and clusters [7]. Modern analytical techniques, as time-resolved fluorescence depolarization and ultra-highresolution mass spectroscopy, allowed to measure the molecular weight of a single asphaltene molecule. It is now believed that the mean molecular weight of an asphaltenic molecule is 750 g/mol [7, 8]. In the literature two main models for asphaltenes structure were proposed: the "island" model and the "archipelago" model. The first describes the asphaltenes as a single polyaromatic core with peripheral alkyl chains. The second describes the asphaltenes as multiple aromatic cores bonded through carbon chains. Currently, thanks to the work of Mullins et al. [7, 9, 10], the "island" model is widely accepted as a reasonable asphaltenes representation.

Many models were proposed to describe pyrolysis of heavy and residual oils in the literature, varying a lot in terms of complexity and data required. Almost all the models present lump species, starting from the simplest one with just two lumps, to complex models that require more computational efforts. Further information about literature available models can be found in the excellent review proposed by Singh et al. [11].

The aim of this work is to build a reliable kinetics scheme to describe pyrolysis of asphaltenes samples following the approach successfully used by Ranzi et al.[12] and Debiagi et al.[13] to model biomasses pyrolysis. The method is based on the definition of a certain number of pseudo-components, each one with a specific pyrolysis pathway. A surrogate mixture is then defined with the linear combination of pseudo components that best approximate a generic asphaltenes sample based on its elemental composition. Having for each pseudo-components a specific reaction pathway, pyrolysis simulations can be performed once the surrogate mixture is described. The main advantage of this approach, with respect to the model proposed in the literature, is to be versatile and fully predictive being able to reproduce the pyrolytic behavior of different asphaltenes samples just knowing their elemental composition. The work was divided into two main steps. The first is the design of suitable pseudo components, and the second concerns the formulation of the kinetics scheme.

## 2. Pseudo-components formulation

The comprehensive description of HFOs pyrolysis is challenging. The main difficulty lies in the impossibility of performing a complete and extensive characterization of the fuel and their SARA fractions. The approach used to characterize asphaltenes fractions follows the methodology proposed by Ranzi and Debiagi et al. [12, 13] to formulate simplified kinetics schemes for biomasses pyrolysis. The idea based on the definition of a certain number of pseudo-components and assign a kinetics pathway to each of them. Samples are then characterized by the linear combination

of pseudo-components that better approximate the actual mixture. The elemental composition (carbon, hydrogen, sulfur, oxygen and nitrogen) is used to discriminate among different asphaltenes, a database with more than 200 data on asphaltenes elemental composition was built. Data on asphaltenes separated from different feedstocks and with different techniques were collected to have an operative range that includes the widest variety of different species. The detailed database can be found elsewhere [14].

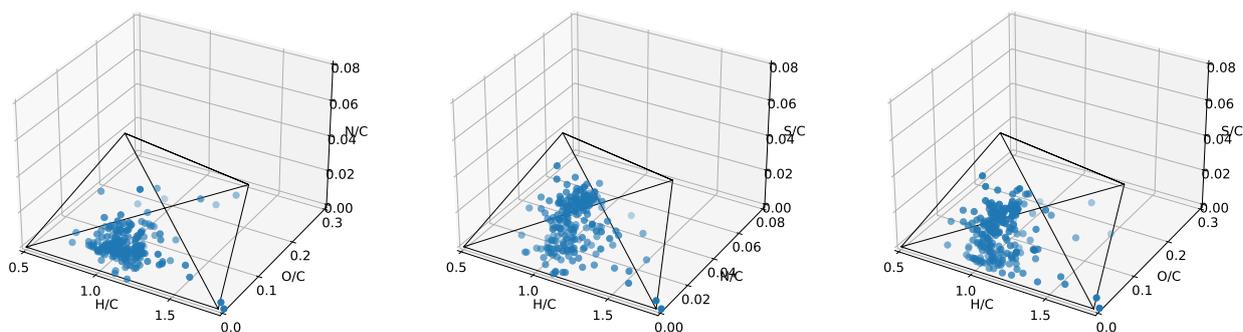


Figure 1: Representation of the graphic approach used to define the atomic ratios of pseudo components. The vertices of the tetrahedrons represent pseudo-components and their atomic ratios. All the experimental data (blue dots) fall inside the tetrahedrons' volume being reconstructible as a linear combination of pseudo components. Data from Guida et al. [14]

The pseudo-components were defined imposing three main constraints. The first one concerns the atomic ratios of each pseudo component, which were selected to be able to reproduce the entire experimental database. To define the suitable atomic ratios of each pseudo components a graphic approach was used. Considering atomic ratio, as the ratio between non-carbon atoms over carbon, the problem results to be a four dimensions problem. Fig 1 reports the 3D projections of the problem. The aim of the graphic approach was to enclose all the experimental data (blue dots) inside the volume of the tetrahedrons. In this way, the entire data set can be reproduced as a linear combination of compounds that lie on vertices. In other words, vertices coordinates return the atomic ratios of each pseudo component. Of course, the decision to follow this graphic approach lies in need to have a model able to reproduce a wide range of experimental data. The second constraint concerns the molecular weight. Asphaltenes' molecular weight was longly debated. Nowadays, the model proposed by Mullins et al. [7, 15] is widely accepted as an accurate representation of asphaltenes structure. According to Mullins, the mean molecular weight of a single asphaltene molecule is  $750 \text{ g/mol}$ . The pseudo components were designed to have a molecular weight, as close as possible, to the mean weight proposed by Mullins. This constraint is necessary to describe the physical behavior of an actual asphaltenes sample having a reasonably close molecular weight. Finally, the third constraint concerns the pseudo components molecular structure. This constraint aims to design pseudo components with structure and groups distribution representative of an actual asphaltenes structure. To accomplish this objective, data from the literature were coupled with in-house experiments performed at KAUST. In particular, Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was performed. An example of experimental information obtain by FT-ICR MS for no heteroatoms compounds is reported in Fig 2. Similar results were also obtained for heteroatoms compounds. Experimental further details can be found here [14]. Where possible, the double bond equivalent (DBE) and carbon number were kept equal to an average of what measured in the FT-ICR MS. Having a pseudo component's structure that is as similar as possible to the actual asphaltenes structure is necessary to develop a reliable kinetics scheme.

Five pseudo components were designed respecting the above-reported constraints. Two of them are pure hydrocarbon with the task to reproduce different features of an asphaltenes molecule. One aims to imitate the aromatic core, mimic an "island structure". The other one represents the alkyl side chains and naphthenic structures generally bonded to the aromatic core. The aromatic core and the side chains were represented separately as two pseudo-components to guarantee flexibility when replicating the H/C ratio of a sample. The two pure hydrocarbon pseudo components do not represent an asphaltene molecule as such, but their combination can potentially describe a hydrocarbon presents

in asphaltenes. The other three pseudo components account for the presence of heteroatoms, one for sulfur, one for oxygen, and one for nitrogen, respectively. These pseudo compounds were designed to be representative of an asphaltenes molecule. The heteroatoms group distribution was defined according to data available in the literature and in-house performed FT-ICR MS.

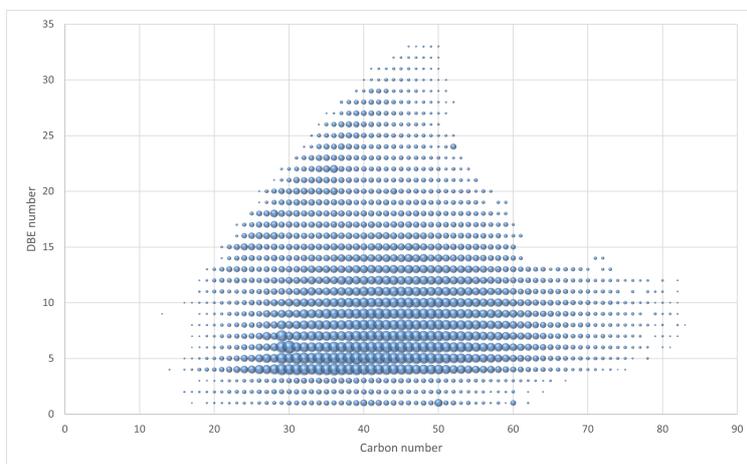


Figure 2: DBE vs Carbon number of no heteroatoms compounds in asphaltenes sample calculated by FT-ICR MS. Bubble size represents the relative abundance. Data from Guida et al. [14]

Asphaltenes generally contain a large amount of sulfur, which is one of the major reason of the huge pollutant release associated with asphaltenes-rich fuels. Two main sulfur groups were identified in the literature, the thioiphenyl and sulfhydryl groups [16, 17]. The sulfuric pseudo component was designed using the information derived from the FT-ICR MS and accounting for the presence of the two sulfuric groups. The length of the side chains and the size of the aromatic core represents the most probable combination of the unsaturation level and number of carbon atoms. In the database, a few asphaltenes contained a large amount of oxygen, reaching a maximum of about 20% by weight. The amount of oxygen in the oxygenated pseudo component was defined according to the high oxygen amount detected experimentally. According to the literature, the hydroxyl and carbonyl functional groups are present [9, 18, 19], as well as, ether groups. Unfortunately, with the FT-ICR MS, is not possible to analyzed oxygenated structure. Therefore, pseudo component structure design followed only the constraints related to the atomic ratio and mean molecular weight. The last pseudo component is the one containing nitrogen. In asphaltenes, nitrogen is present essentially in the pyridinic form [20]. Again the design derived from the combination of FT-ICR MS experiments and literature data. For detailed information about pseudo components structure, please refer to Guida et al. [14].

Given the elemental characterization of an asphaltenes sample, it is possible to define the linear combination of pseudo components that best approximate the sample by solving the five atomic balances.  $\alpha, \beta, \gamma, \delta$  and  $\epsilon$  represents the unknown mass fractions of the reference species, while  $w_j^i$  is the mass fraction of the  $j$ -th element in the  $i$ -th reference species.  $w_j^{Sample}$  is the mass fraction of  $j$ -th element in the sample according to elemental analysis.

$$\alpha * w_C^1 + \beta * w_C^2 + \gamma * w_C^3 + \delta * w_C^4 + \epsilon * w_C^5 = w_C^{Sample} \quad (1)$$

$$\alpha * w_H^1 + \beta * w_H^2 + \gamma * w_H^3 + \delta * w_H^4 + \epsilon * w_H^5 = w_H^{Sample} \quad (2)$$

$$\alpha * w_N^1 + \beta * w_N^2 + \gamma * w_N^3 + \delta * w_N^4 + \epsilon * w_N^5 = w_N^{Sample} \quad (3)$$

$$\alpha * w_S^1 + \beta * w_S^2 + \gamma * w_S^3 + \delta * w_S^4 + \epsilon * w_S^5 = w_S^{Sample} \quad (4)$$

$$\alpha * w_O^1 + \beta * w_O^2 + \gamma * w_O^3 + \delta * w_O^4 + \epsilon * w_O^5 = w_O^{Sample} \quad (5)$$

### 3. Kinetics scheme

Once the pseudo components and the characterization method were designed, the following step was the development of the kinetics scheme. A reaction pathway is associated with each pseudo component. Pyrolysis is a complex phenomenon involving a large number of different reactions and species, following complicated pathways. Reactions as  $\beta$ -scission, ring opening, isomerization, dehydrogenation, hydrogen shuttling are expected to occur, other than, condensation reactions which progressively enhance the number of fused rings leading to the formation of solid products (CHAR). Due to its complexity, it is not possible, at least at the actual stage, to model pyrolysis in detail considering all the reactions mentioned and their competition. The kinetics scheme was developed to be as simple and general as possible while reasonably accurate. The pyrolytic behavior of each pseudo component is modeled with a first-order irreversible reaction with the task to approximate the overall kinetics. Each reaction leads to the formation of gas and solid (CHAR) products. Generally, during pyrolysis, the sample mass loss is driven by the competition between two phenomena, pyrolysis reactions, and evaporation. However, asphaltenes have a sufficiently high boiling point to ensure they remain in the liquid phase during cracking reactions, as proofed by Alshareef et al. [21] using model compounds to mimic asphaltenes reactivity.

Gas and solid products are considered in the model. The solid products are called CHAR. The formulation of the kinetics scheme proceeded through chemistry-related considerations and experimental information intending to reproduce the significant pyrolysis products. In particular, the model predicts the formation of small hydrocarbons as hydrogen, methane, saturated and unsaturated hydrocarbons up to C6. Where C4, C5, C6 compounds are lumped species to account for linear and branched hydrocarbons. Cyclohexane and cyclohexene are considered too, other than, small aromatics compounds as benzene, toluene, xylene, ethylbenzene, styrene and methyl-naphthalene. A compound with ten carbon atoms ( $C_{10}H_{20}$ ) is also present as lumped species representing all hydrocarbons heavier than C6. Even if no aromatics compounds attached to alkyl chains are present in pseudo components molecules, the formation of aromatics products is expected and observed. Indeed, small aromatics attached to allyl chains can be present in the actual asphaltenes or formed due to Diels–Alder reactions [22]. Also, heteroatoms products are expected. In the kinetics scheme, carbon monoxide and carbon dioxide are present as oxygenated species. Hydrogen cyanide is used as lump species to account for all the nitrogenated gases. Sulfur gas products are represented by hydrogen sulfide and benzo-thiophene. Benzo-thiophene is representing all the heavier sulfuric species released during pyrolyses such as thiophenes, benzothiophenes, dibenzothiophenes and all the alkyl-substituted homologs [17]. Five species describe solid products. The sum of these five species returns the solid residue remaining after pyrolysis. Three of them account for the presence of heteroatoms in solid residue.  $CHAR_S$ ,  $CHAR_N$ ,  $CHAR_O$  are used to describe the presence of sulfur, nitrogen and oxygen, respectively in the solid residue.  $CHAR_H$  accounts for the presence of hydrogen, whilst  $CHAR$  represents the presence of carbon. For detailed information about the kinetics scheme, please refer to Guida et al. [14].

#### 3.1. Kinetics parameters

Finally, to complete the kinetics scheme, parameters such as products stoichiometric coefficients, activation energy, and pre-exponential factor of each reaction were tuned. Kinetics parameters were tuned using a fitting data approach. Generally, thermogravimetric analysis (TGA) is used experimentally to perform pyrolysis studies. TGA allows estimating the sample mass loss rate and the amount of solid residue obtained by the thermal decomposition process. Due to model assumptions, CHAR stoichiometric coefficients, pre-exponential factors, and activation energies are the only parameters influencing the sample mass loss in the model. Pre-exponential factors and activation energies characterize the mass loss rate and the temperature at which it occurs, while CHAR stoichiometric coefficients determine the amount of solid residue. Therefore, these parameters were tuned to match the experimental information obtained by TGA experiments, both from the literature and in-house performed. Gas products stoichiometric coefficients were tuned with a fitting data approach to match experimental evidence. Kinetics constant parameters and stoichiometric coefficients were tuned separately using two different optimization procedures. Kinetics constant parameters were tuned using as optimization tool the function *lsqcurvefit* in @MATLAB 2020b software package. While, both gas and solids stoichiometric coefficients were tuned manually in @Excel. The optimization was performed imposing the atomic balances as constraints with the objective to minimize the least-square error obtained by the difference through model predictions and the entire pool of experimental data. Again, further details can be found in the work of Guida et al. [14].

## 4. Results

### 4.1. TGA simulations

Fig3 reports the comparison between model simulations and TGA experiments performed on asphaltenes from different origins and separated with different techniques. The grey shaded area displayed around the measured value accounts for a measure uncertainty of 8%. The experimental data were found in the literature. One refers to an asphaltenes sample extracted from Athabasca oil sands. Athabasca sample elemental composition and experimental TGA curve can be found et al. [23, 24], respectively. The other sample refers to asphaltenes extracted from vacuum residue obtained by Chinese Liaohe crude oil [25].

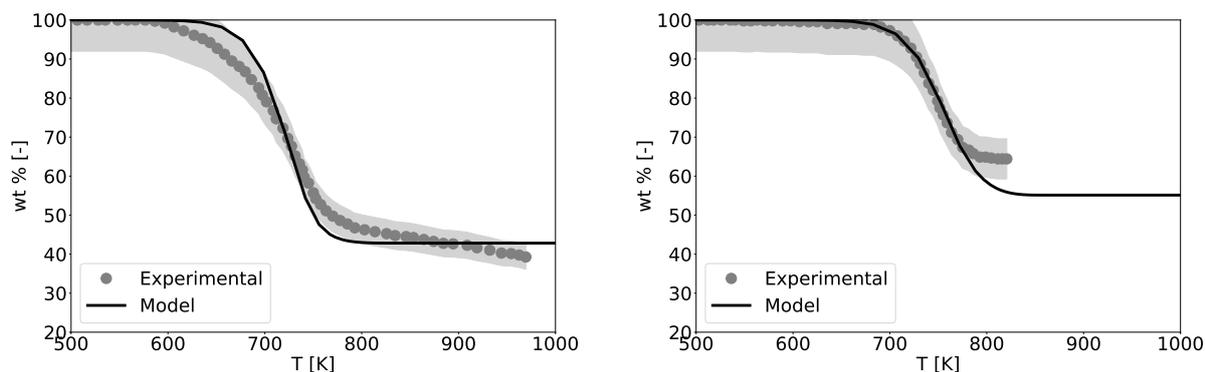


Figure 3: Comparison between model simulation and TGA experiments. Asphaltenes extracted from Athabasca oil sands on the left, asphaltenes extracted from Liaohe vacuum residue on the right. An uncertainty of 8% is displayed as the shaded area around the measured value.

Fig3 shows clearly that the model captures the differences between the two samples reproducing with reasonable accuracy both the samples. The difference in simulation results derived from the definition of different surrogate mixtures based on samples' elemental composition. The definition of the surrogate mixture influences both the region of the decay curve and the final solid residue amount. The agreement between model predictions and experimental data confirms that the elemental composition is an adequate parameter to discriminate among different asphaltenes. Therefore, the strong point of the model is the ability to discriminate among different samples, being fully predictive just knowing the sample's elemental composition. Other comparisons between model and experimental data can be found et al.[14].

### 4.2. Gas products distribution

The final part of the work consisted of the definition of the gas products distribution. Detection of gaseous species produced during pyrolysis is not trivial as many species are involved, and their detection is not always possible. Different techniques can be used for products detection. TGA coupled with Fourier transform infrared spectroscopy (TG-FTIR) allows the online detection of products. Some authors recently, reported results of TGA-FTICR for asphaltenes pyrolysis [26, 27]. However, TGA-FTICR results are helpful to improve knowledge about asphaltenes pyrolysis. Still, they cannot be used for quantitative consideration being reported in terms of absorbance and not the concentration of species. A methodology to obtain quantitative data consists of calibrating instruments for the detection of specific species. Speight et al.[28] and Ritchie et al.[23] reported quantitative data about hydrogen, methane, carbon monoxide, carbon dioxide, and other small hydrocarbons from asphaltenes pyrolysis. Another way to detect gas products after pyrolysis is coupling the pyrolysis apparatus with gas chromatography and mass spectroscopy analysis. Zhang et al. [17] performed fast pyrolysis experiments of asphaltenes extracted from an Iranian vacuum residue reporting the percentage hydrocarbon distribution for pyrolysis products including alkanes, alkenes, cycloalkanes, cycloalkenes, alkadienes, aromatics, and sulfur compounds. Unfortunately, low molecular weight components, such

as methane and hydrogen, were not detected. Model parameters were tuned fitting the few experimental data available. In particular, data from Zhang et al. [17], Speight et al.[28], and Ritchie et al.[23] were used, being the only quantitative data found in the literature suitable to be reproduced by the model under development. One more set of experimental data used, comes from in-house experiments performed at KAUST. A detailed comparison between model results and experimental data can be found in work of Guida et al. [14].

## 5. Conclusion and future developments

This work presents the methodology used to develop a kinetics scheme for asphaltenes pyrolysis. First of all, a characterization framework was defined based on the design of five pseudo components to generate surrogate mixtures. Pseudo components were defined to describe the entire database with 208 different samples collected from the literature. Then, a pyrolysis reaction pathway was assigned to each pseudo component based on chemistry-related considerations derived from their structures. Kinetics parameters of each reaction, as well as, the stoichiometric coefficients of solid products, were tuned to match experimental information from TGA experiments. On the other hand, gas products' stoichiometric coefficients were tuned to fit three sets of experimental data from the literature and one from in-house experiments. The kinetics scheme is able to reproduce with reasonable accuracy the data about the gas products distribution, as well as, decay rate and solid residue from TGA experiments. The good accuracy obtained allows to state, with reasonable confidence, that discriminating molecules and relative kinetics evolution on elemental composition is a reasonable approach to have a general yet accurate estimation of pyrolysis rate and released products. The model obtained is predictive and versatile being able to reproduce the pyrolytic behavior of different asphaltenes samples just knowing their elemental composition. On the basis of the good results obtained for asphaltenes, an analogous model is under development also for resins fractions.

The work is part of a comprehensive project that aims to develop a model able to reproduce the pyrolytic behavior of each SARA (Saturates, Aromatics, Resins, Asphaltenes) fraction and to reconstruct the HFOs pyrolytic behavior as a combination of its fractions contribution. The kinetics scheme proposed for asphaltenes represents a first step in the formulation of a comprehensive kinetics scheme for HFOs, which can be adopted for design, tuning, and optimization of unit operations in combustion and gasification applications.

## 6. Acknowledgments

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