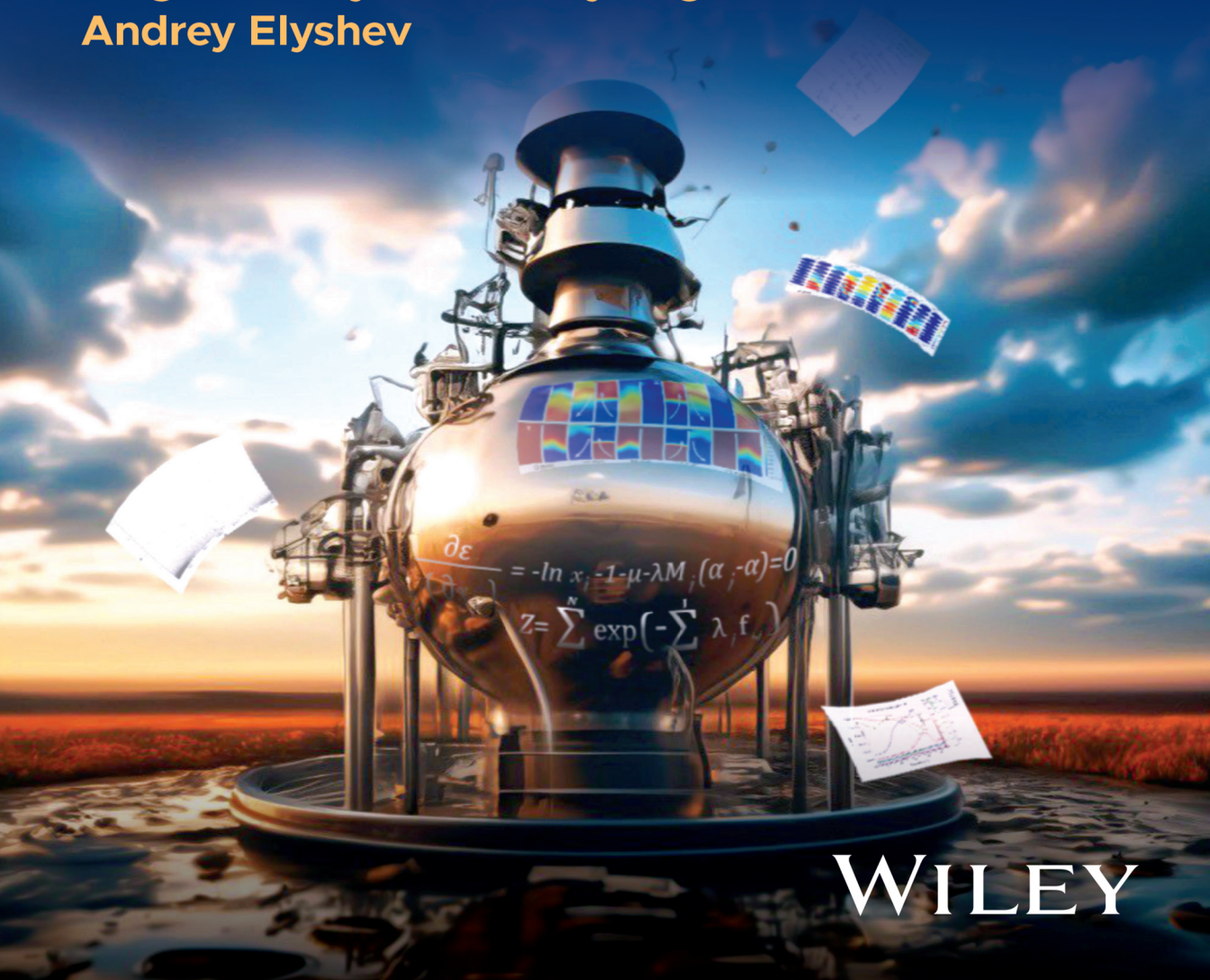
Mathematical Modeling of Complex Reaction Systems in the Oil and Gas Industry

Edited by
Jorge Ancheyta • Andrey Zagoruiko
Andrey Elyshev



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Edited by

Jorge Ancheyta
Instituto Mexicano del Petróleo
Mexico City, Mexico

Andrey Zagoruiko
Boreskov Institute of Catalysis
Novosibirsk, Russia

Andrey Elyshev
University of Tyumen
Tyumen, Russia

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Contents

List of Contributors

Osman Abdulla
Tyumen State University, Tyumen, Russia

Jorge Ancheyta
Department of Petroleum Engineering
Kazan Federal University, Kazan, Russia;
Instituto Mexicano del Petróleo
Mexico City, Mexico; and Escuela Superior de
Ingeniería Química e Industrias Extractivas
Instituto Politécnico Nacional, UPALM
Zacatenco, Mexico City Mexico

Cristian Calderón
Tecnológico de Monterrey, Mexico State
Mexico

Andrew Elyshev
Tyumen State University, Tyumen, Russia

Guillermo Félix
Department of Petroleum Engineering
Kazan Federal University, Kazan
Russia and Tecnológico Nacional de
México/IT de Los Mochis, Los Mochis
Sinaloa, Mexico

Nikita Glazov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrent'yeva
5, Novosibirsk, Novosibirsk Oblast
Russian Federation

Javier Jurado
Instituto Politécnico Nacional, Centro de
Investigación en Ciencia Aplicada y Tecnología
Avanzada, Unidad Legaria, Legaria 694
Col. Irrigación, Ciudad de México, Mexico

Sergey Lopatin
Boreskov Institute of Catalysis, Novosibirsk
Russia and Tyumen State University
Tyumen, Russia

César I. Méndez
Centro de Investigación en Ciencia Aplicada
y Tecnología Avanzada del Instituto Politécnico
Nacional, Mexico City, Mexico

Alexis Tirado
Department of Petroleum Engineering
Kazan Federal University, Kazan, Russia

Fernando Trejo
Instituto Politécnico Nacional
CICATA–Legaria, Ciudad de México, Mexico

Andrey Zagoruiko
Boreskov Institute of Catalysis, Novosibirsk
Russia and Tyumen State University
Tyumen, Russia

Sergey Zazhigalov
Boreskov Institute of Catalysis, Novosibirsk
Russia and Tyumen State University
Tyumen, Russia

Vicente Samano
Instituto Politécnico Nacional
Centro de Investigación en Ciencia
Aplicada y Tecnología Avanzada
Unidad Legaria, Legaria 694
Col. Irrigación
Ciudad de México, Mexico

Preface

After more than 30 years of experience working in the kinetic and reactor modeling of different processes for the petroleum and gas industry as well as for environmental protection applications, we have identified the need to have a collection of the most relevant cases that would have great impact on the industry. The general areas that are described in this book correspond to reaction kinetics, catalyst deactivation, reactor model, computational fluid dynamics, and steady-state and dynamics simulations using own experimental data or information reported in the literature.

Mathematical Modeling of Complex Reaction Systems in the Oil and Gas Industry is focused on the step-by-step description of kinetics and reactor modeling of various important processes used in the oil and gas industry. The topics covered in this book are hydrocracking of heavy oils, catalyst deactivation, oxidative regeneration of catalyst, adsorption–desorption catalytic processes, molecular reconstruction, production of green diesel via catalytic hydrotreating, slurry-phase hydrocracking reactor, Fischer–Tropsch synthesis and structured beds of micro-fibrous catalyst. Nowadays, all these topics are relevant to the oil and gas industry, particularly in this era of energy transition and decarbonization, which makes the book original and unique among previous reactor modeling books.

Each chapter describes the development of kinetic and reactor models for steady-state and dynamic simulations. To develop the kinetic model for each reaction or set of reaction for further reactor modeling, exhaustive experimental data either reported in the literature or generated in own laboratories are used. The developed models are validated with laboratory experimental data and simulation are reported to predict the commercial performance of the involved reactors. In addition, such a modeling in some cases allows for a deeper understanding of the qualitative essence of the phenomena observed in experiments, that is, to apply the augmented reality approach and make visible what cannot be directly observed in experiments, or at least to reproduce the most plausible picture of the physical events taking place.

This book is expected to be a reference guide for researchers, PhD students, postdoctoral researchers, catalyst manufacturers, process designers, and professors, to help them develop kinetic and reactor models at different reaction scales. It is also anticipated that this textbook can be used to cover part of the content of courses of different carriers at undergraduate and postgraduate levels.

Jorge Ancheyta, National Polytechnic Institute and Mexican Institute of Petroleum, Mexico
Andrey Zagoruiko, Boreskov Institute of Catalysis, Novosibirsk, Russia
Andrey Elyshev, Tyumen State University, Russia

1

Modeling the Kinetics of Hydrocracking of Heavy Oil with Mineral Catalyst

Guillermo Félix[1,2], Fernando Trejo[3], and Jorge Ancheyta[4,5]

[1] *Department of Petroleum Engineering, Kazan Federal University, Kazan, Russia*
[2] *Tecnológico Nacional de México/IT de Los Mochis, Los Mochis, Sinaloa, Mexico*
[3] *Instituto Politécnico Nacional, CICATA-Legaria. Legaria 694, Col. Irrigación, Ciudad de México, Mexico*
[4] *Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, San Bartolo Atepehuacan, Mexico City, Mexico*
[5] *Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, UPALM, Zacatenco, Mexico City, Mexico*

1.1 Introduction

The continuously increasing global demand for energy and the decrease of light crude oil reserves have caused researchers to look toward heavy crude oil reserves. Despite the importance of renewable sources is growing, fossil energy sources will continue to meet most of the global energy requirements (Bellussi et al. 2013; Félix and Ancheyta 2019a; Martínez-Grimaldo et al. 2014; Rana et al. 2007; Santos et al. 2014). The driving forces of the oil industries to improve heavy crude oils and vacuum residues (VRs) are as follows: (i) obtain high-quality transportation fuels, (ii) middle distillates, (iii) reduction of conventional crude oil supply, and (iv) price increase. Heavy crude oils or VRs are considered suitable alternative sources for transportation fuels, energy, and petrochemicals to meet the demands of industries. However, because of the low quality and difficulties in transporting heavy crude oils, it is necessary to develop technologies to upgrade their properties (Castañeda et al. 2014; Martínez-Grimaldo et al. 2014; Sahu et al. 2015).

In recent decades, researchers have prioritized refining techniques that use low-cost feedstock, such as coal, low-grade oil or wax, heavy crude oil, VRs, and natural gases, which are aimed to improve the cost-effectiveness of the refining process. The goal of these techniques is to transform such feedstock into transportation fuels and other low-boiling point liquid products. Refining heavy crude oils and VRs decreases their viscosity, initial boiling point, metal contents, sulfur, and other impurities, while increasing the H/C ratio to meet the commercial standards (Rodríguez et al. 2018; Sahu et al. 2015; Speight 2004).

1.1.1 Reserves and Production of Heavy Crude Oils

The assessment of production capacity of oil field reveals that conventional light and medium oil reserves peaked in the 1960s. Since then, these reserves have steadily declined. An important focus of the global oil industry is to develop new technologies to be feasible: the use of unconventional resources as heavy and extra heavy crude oils (Heidary et al. 2017; Martínez et al. 2010; Santos et al. 2014). At the end of 2021, more than 1730 billion barrels of proven reserves are reported worldwide,

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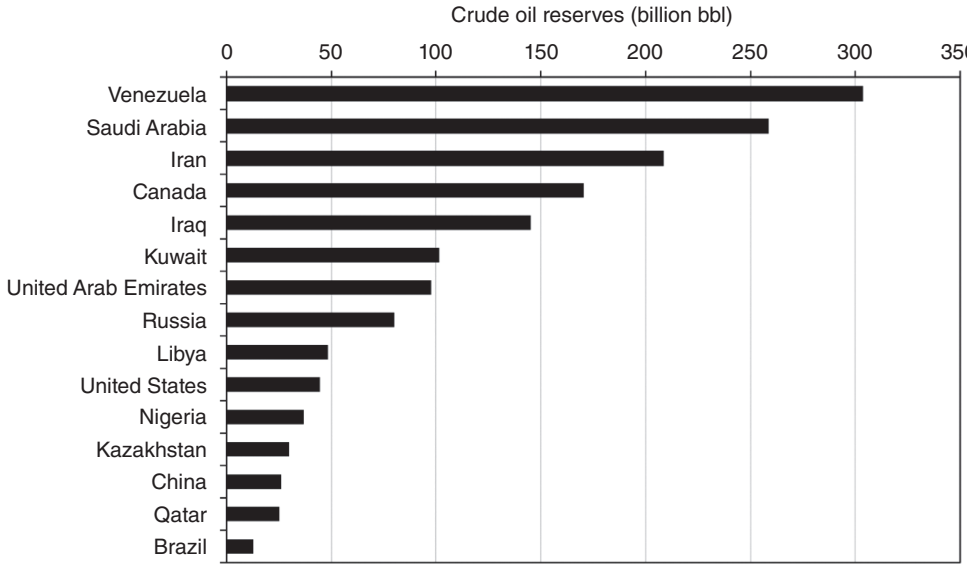

Figure 1.1 Proven reserves of crude oil by country.

as shown in Figure 1.1 (*International—U.S. Energy Information Administration (EIA)* 2021; *Oil Gas Journal* 2022; *Organization of the Petroleum Exporting Countries (OPEC)* 2020). Venezuela, Saudi Arabia, and Iran possess the largest crude oil reserves; however, the quality of their crudes varies significantly. Currently, these reserves contain 434.3 billion barrels of heavy and extra-heavy crude oil, while 650.7 billion barrels correspond to bitumen, representing over 60% of the total volume (Bata et al. 2019; Pratama and Babadagli 2022).

1.1.2 Heavy Crude Oil Upgrading Processes

The processing of the heavy crude oil presents difficulties due to the complex nature of its heavier fractions, which commonly possess low API gravity (high density), high viscosity, elevated initial boiling point, higher contents of heteroatoms (sulfur, nitrogen, and oxygen), metals (Ni and V), and asphaltenes. In general, most of sulfur and nitrogen species present in crude oils are found in heavier fractions, while metals are found in porphyrins and as concentrated, exclusively in residue fractions (Ancheyta 2011; Memon et al. 2010; Quitian and Ancheyta 2016b). Therefore, the addition of hydrogen or rejection of carbon is the main process focused to increase the hydrogen-to-carbon (H/C) ratio in heavy crudes. These two routes can be catalytic and noncatalytic (Ancheyta 2013; Félix et al. 2017).

Over the years, several technologies based on carbon rejection, the addition of hydrogen, and the combination of both have been used to upgrade heavy crude oils (Figure 1.2). The noncatalytic (deasphalting, gasification, coking, and visbreaking) and catalytic (catalytic cracking of VR) carbon rejection technologies account for 56.6% of the global processing technology due to its cost-effective operation. The noncatalytic (hydrovisbreaking) and catalytic (hydrotreating and hydrocracking) hydrogen addition technologies display advantages and disadvantages when applied to heavy crude oil processing as well as carbon rejection technologies (Castañeda et al. 2014; Rana et al. 2007; Sahu et al. 2015; Speight 2004).

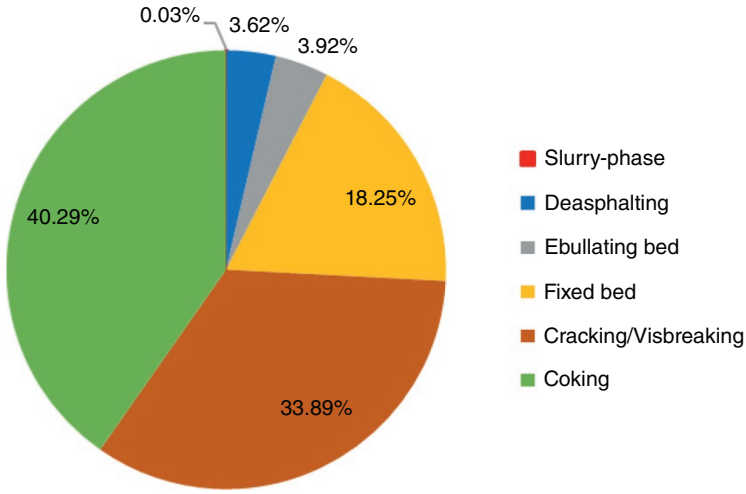

Figure 1.2 Processing capacity for worldwide heavy crude oil upgrading technologies.

For heavy and extra-heavy crude oils, the choice between carbon rejection and hydrogen addition technologies depends on technical and economic assessments, as well as the quality of products from downstream refining processes. Therefore, deciding on which upgrading technology is appropriate for certain heavy crude oil is not an easy task and several factors must be taken into consideration, such as the following (Ancheyta 2013; Ancheyta and Speight 2007; Quitian and Ancheyta 2016b):

✓ Price of heavy crude oil
✓ Amount of impurities in feedstock
✓ Level of quality of the upgraded oil
✓ Process outline of the refinery

In the past, the carbon rejection technologies were preferred for feed with high metal content, such as heavy crude oils. Nonetheless, these technologies have the following disadvantages (Ancheyta 2013; Sahu et al. 2015):

✓ Low yield of upgraded oil
✓ Enhanced formation of coke
✓ High aromatic content in the upgraded oil
✓ Lower yield and quality of gasoline and diesel fuels
✓ Low value of upgraded oil

Technologies based on the hydrogen addition produce crude oils that possess superior quality and greater added value than carbon rejection methods do; hence, these approaches are becoming increasingly attractive. Highlights of the hydrogen addition technologies are the following:

✓ Minimizes the coke formation
✓ Enhances the yield of liquid products obtained by hydrocracking or hydrogenolysis mechanisms
✓ Increases the H/C ratio of the products
✓ Reduction of impurities, such as sulfur, nitrogen, metals, and asphaltenes
✓ Increases hydrogen consumption, giving higher liquid yields

These technologies also present the following disadvantages (Ancheyta 2013; Quitian and Ancheyta 2016b; Rana et al. 2007):

- ✓ Large volumes of hydrogen are necessary to carry out the hydrogenation of carbon-rich crude oil
- ✓ Difficulties arise from the carbon and metal deposition on the catalyst surface
- ✓ Requires well-designed catalysts that are able to process high levels of metals and asphaltenes within the feed

There are also some emerging technologies at different levels of development or even close to be commercialized, which have been developed due to the growing production of heavy and extra-heavy crude oils (Castañeda et al. 2014; Speight 2004). Hydrocracking is a well-known refining process where heavy crude oil in hydrogen atmosphere is transformed into light products with better quality. There are different types of reactors to carry out this process and the choice depends mainly on the level of conversion required and the number of impurities (metals and asphaltenes) in the feed. Three-phase catalytic reactors are highly valued due to their broad applications in various reaction systems and being notably used in the petroleum industry, including hydrocracking processes. Fixed-bed reactors have stable and reliable performance, but strong limitations are feed properties due to fast catalyst deactivation by coking and metal depositions. Ebullated-bed reactors perform better than fixed-bed reactors since they can process feed containing higher quantities of metals and coke at the expense to be conversion-limited and reaching values up to 80%. This is because of the rapid formation of sediments, by which commonly aromatic solvents are used to keep the soluble in the reacting phases. Slurry phase reactors achieve higher conversions performing superior levels of upgradation of feed rich in sulfur, metals, and asphaltenes (Ancheyta 2011; Jarullah et al. 2011; Martínez-Grimaldo et al. 2014; Sahu et al. 2015).

The degree of conversion is affected by the properties and nature of the feed, thus lighter crude oil possesses lower number of impurities, while heavy fractions contain higher content of asphaltenes (Alonso et al. 2019; Marafi et al. 2005; Ortega-García et al. 2012; Stanislaus et al. 2005; Stratiev et al. 2014, 2019; Tirado and Ancheyta 2018). Asphaltene is the most polar fraction found in heavy crudes and residues that is soluble in aromatic solvents but not in alkanes. This fraction comprises of both aromatic and aliphatic carbons, which contribute to its high molecular weight. The complex structure (Figure 1.3) makes asphaltenes one of the most studied fractions as they are coke precursors. The asphaltene fraction is formed by large aromatic sheets, side alkyl chains, heteroatoms, and metalloporphyrins. These latter components exhibit a remarkable influence of p-electronic interactions. The alteration in solubility during the processing of heavy crudes or residues is linked to solid formation. This disruption in solubility equilibrium relies on the chemical characteristics of the feed and the processing conditions. Based on the colloidal model (Figure 1.4), asphaltenes are surrounded by resin-building micelles keeping the asphaltenes dispersed in crude oil that avoids the contact with saturated compounds, since their nonpolar nature cause the instability of asphaltene micelles. Sediment formation is the result of a disturbance in the balance between asphaltenes and those compounds that keep them dispersed in solution during hydrotreating/hydrocracking; in other words, resins lose their peptization properties causing aggregation and precipitation of asphaltenes (Ashoori et al. 2017; Félix and Ancheyta 2019a; Ortega-García et al. 2012; Rana et al. 2007; Rogel et al. 2013; Stratiev et al. 2014, 2019; Tirado and Ancheyta 2018).

In addition to the loss of solubility of asphaltenes by oil and resin fractions, hydrocracking leads to an increase in the aromaticity and condensation of unconverted asphaltene cores. Reports indicate that the asphaltenes found in upgraded products have higher aromaticity and a lower H/C ratio in comparison with original asphaltenes in the feed. The results of structural analysis of the hexane-insoluble fraction indicate a higher degree of polarity due to the presence of a significant number of

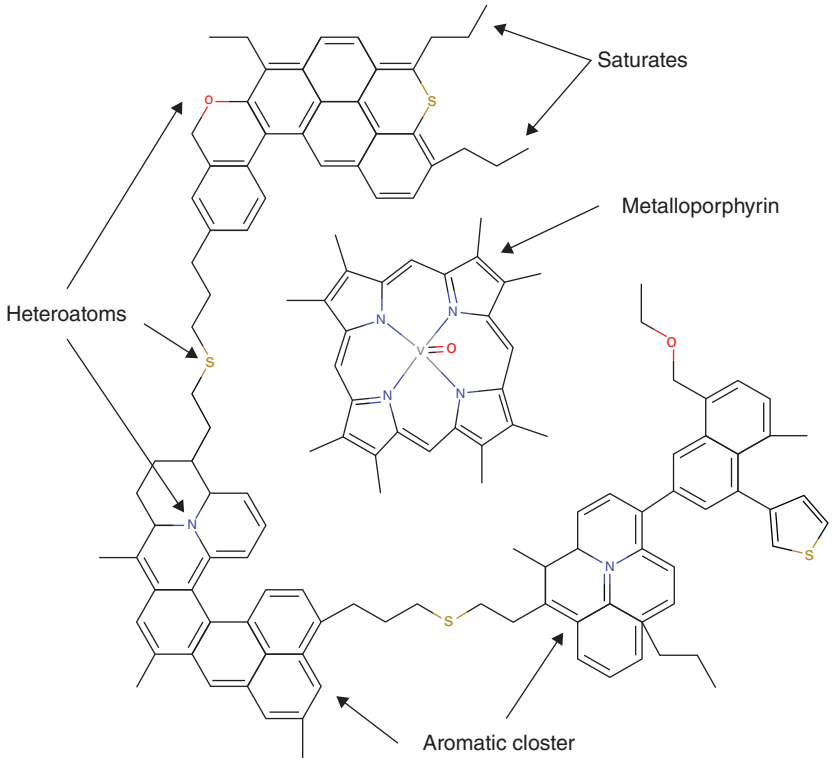

Figure 1.3 Hypothetical asphaltene molecule.

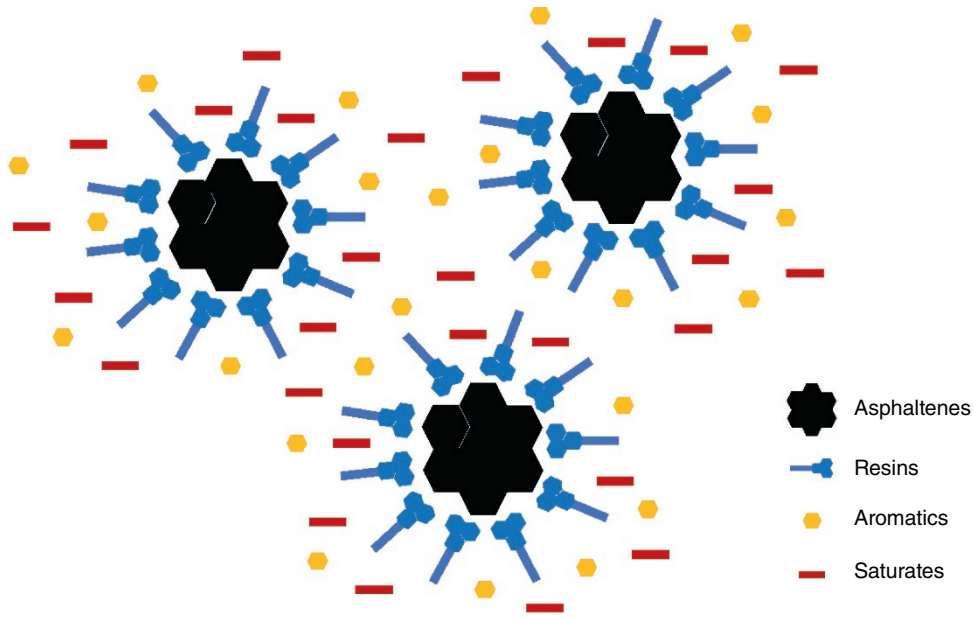

Figure 1.4 Heavy crude oil composition based on SARA fractions.

heteroatoms with shorter alkyl chains because of the dealkylation reactions, which causes asphaltenes to become more aromatic and precipitate. The precipitation of sediment has also been attributed to the possible liquid–liquid phase separation of the material at high temperatures of processing (Mochida et al. 1989; Rogel et al. 2013; Tirado and Ancheyta 2018).

Sediment formation typically has a maximum limit of 0.8–1.0 wt.% in refineries. Higher values may cause commercial plants to shut down due to plugging issues. For this reason, sediment formation is a critical process parameter during hydrotreating and hydrocracking of heavy oils and thus dictates the maximum allowable residue conversion. Furthermore, a more extensive comprehension of sediment formation during upgrading processes is essential for enhancing both performance and control strategies. Improving the predictability of sediment deposition is highly desirable as it would enable the preliminary screening of feed and the optimization of processing (Alonso et al. 2019; Rogel et al. 2013; Tirado and Ancheyta 2018).

1.1.3 Reactions During Slurry Phase Hydrocracking

For hydrocracking reactions in slurry phase, the operating conditions can be classified as follows (Quitian and Ancheyta 2016a; Speight 2013):

- Mild conditions can be attained if the pressure and temperature do not exceed 80–100 kg/cm^2 and 410 °C, respectively, while the hydrocracking of heavy crude oil or residua leads to a VR of less than 50%.
- Severe conditions are reached at pressure and temperature exceeding 80–100 kg/cm^2 and 410 °C, respectively, and the VR conversion is greater than 50% during the hydrocracking of heavy crudes or residua.

Hydrocracking and hydrogenolysis are exothermic reactions and may occur at different extents depending on the operating conditions. At mild temperatures, hydrogenation is the dominant reaction unlike hydrocracking and thermal cracking reactions that take place at high temperatures (Quitian and Ancheyta 2016a; Raşeev 2003). The polyaromatic compounds break the weak bonds, such as C–S, C–O, and so on, and transform into free radicals. Meanwhile, the H_2 molecule dissociates to form Mo–H or S–H bonds, which in turn release hydrogen radicals to cap unstable compounds. Consequently, the formation and saturation of free radicals is a cyclic process. It has been reported that thermal and catalytic hydrocracking occur in series, the residue is converted to vacuum gas oil (VGO), medium distillate, naphtha, and gases, and the combination of thermal cracking and hydrogenation promotes the formation of the requested products (Martínez-Grimaldo et al. 2014; Nguyen et al. 2016; Quitian et al. 2015).

1.1.4 Catalysts for Hydrocracking of Heavy Crude Oils in Slurry Phase

The types of catalysts used in hydrocracking process are the solid heterogeneous powders and dispersed catalysts. The first type contains at least one metal (cobalt, molybdenum, nickel, iron) supported on alumina, silica–alumina, etc., by which the catalytic system is heterogeneous, containing the feed in liquid phase, the hydrogen in gaseous phase, and the catalyst in solid phase. As the reaction takes place, heavier molecules block the pore mouths and reduce the catalytic activity, thereby, reducing the reaction rate (Nguyen et al. 2016; Rodríguez et al. 2018). To solve this issue, unsupported catalysts were developed. The dispersed catalysts are particulate materials that enhance the catalytic hydrotreating at high reaction rates due to their large specific surface area, which makes the kinetics in the slurry phase faster than in fixed-, moving-, or ebullated-bed reactors. The faster

the mass and energy transfer, the lower the over-hydrocracking activity, and thereby, the lower the coke and gas formation (Liu et al. 2009; Quitian and Ancheyta 2016a).

Dispersed catalysts are highly stable by which optimized contact between oil and hydrogen is possible. As a result of high metal contents in dispersed catalysts, the heavy hydrocarbons reach the active sites very quickly and avoid plugging the pores as in supported catalysts. For these reasons, dispersed catalysts can be used directly in presence of heavier feedstock making slurry processes more suitable than other hydroconversion technologies when processing heavy feedstock (Angeles et al. 2014; Bellussi et al. 2013). Dispersed catalysts consist in different types: (i) soluble in water, (ii) soluble in oil (in this case heavy crude oil), (iii) mineral, and (iv) ionic liquid. The dispersed oil-soluble catalysts are generally more expensive than the water-soluble catalysts, but the water can evaporate during the reaction and reduce the catalytic activity, resulting in particle agglomeration. Meanwhile, the oil-soluble catalyst can be uniformly dispersed in the feed enhancing hydrogen uptake and suppressing the coke formation. The conversion as well as the quality of liquid product increases (Galarraga et al. 2012; Kim et al. 2017; Liu et al. 2009; Nguyen et al. 2016).

The mineral catalysts are natural ores with a high content of one or more transition metals, usually the Fe-based and Mo-based minerals are the most employed for slurry-phase hydrocracking. Different works have been employed magnetite, limonite, hematite, ferrite, laterite, pyrite, and molybdenite, among others. This type of catalyst does not require any special preparation, instead drying, grinding, and sieving are the usual operations required before using, making them cheaper than other catalysts (Al-Attas et al. 2019; Fukuyama and Terai 2007; Quitian and Ancheyta 2017). The ionic liquid catalysts are a relatively new alternative to dispersed catalysts. These compounds are organic salts that can be liquefied at near room temperature. Their catalytic activity depends primarily on the cations and anions used during synthesis and usually contain molybdenum, cobalt, iron, or nickel (Cai et al. 2022; Ma et al. 2022). It is preferred to use molybdenum compounds as dispersed catalysts due to their greater hydrogenation activity (Calderon and Ancheyta 2016; Du et al. 2015; Panariti et al. 2000). It has been shown that metal sulfide is the active species in hydrocracking process, and it is formed by reacting the metal precursors with sulfur compounds in the feed or additional sources of sulfur (Nguyen et al. 2016; Panariti et al. 2000). The sulfidation (activation of catalysts) is done before the hydrocracking reaction and starts by two routes: (i) *ex situ* and (ii) *in situ* sulfidation. In the case of *ex situ* sulfidation, the sulfur sources are often found in carbonaceous compounds (as heavy crude oils) or using hydrogen sulfide (Nguyen et al. 2016; Quitian and Ancheyta 2016a). Small concentration of low-cost, finely dispersed catalyst makes recovery impractical after reaction. In addition, slurry catalysts are deactivated after reaction, which occurs by coke and metal deposition hindering its reuse (Quitian and Ancheyta 2016a; Rezaei 2013).

1.2 Kinetic Models

For adequate modeling of a new hydrocracking process is imperative to take into account the feed properties, design, performance, process control, and cost to meet the specification of the products. The main issue when modeling hydrocracking process is the complex nature of feedstock compared with model compounds by which it is necessary to understand the changes in the rate constants, conversion, and API gravity at different reaction scales. This will improve the methodologies for upscaling reaction parameters from the laboratory to industrial scale (Ancheyta et al. 2005; Becker et al. 2016; Celse et al. 2015; Elizalde et al. 2009; Hassanzadeh and Abedi 2010; Marafi et al. 2010; Rashidzadeh et al. 2011).

1.2.1 General Types of Kinetic Models

Discrete and continuous lumping models have been largely used to represent the reaction kinetics. Recently, the use of more complex and fundamental microkinetic models to simulate hydrocracking has increased the interest of the research community (Becker et al. 2016; Martínez and Ancheyta 2012; Sánchez et al. 2005a). The yield of gases, naphtha, middle distillates, VGO, and residue based on boiling point intervals is adequately predicted by kinetic models. In addition, the so-called SARA fractions, that is, saturates, aromatics, resins, and asphaltenes, are also included in the modeling. Kinetic studies for the transformation of asphaltenes into maltenes fractions (saturates, aromatics, and resins) have received less attention than those involving the pseudocomponents based on boiling point ranges (Asaee et al. 2014; Félix and Ancheyta 2019a; Moustafa and Froment 2003).

1.2.1.1 Lumping Kinetic Models

Traditional models by pseudocomponents take macroscopic properties (for example, measurable properties in the product) and derive the equation system to be solved. These models can be specifically grouped into compounds in the feed or products in a few cuts, often characterized by ranges of boiling points that undergo different reactions in series or parallel (Ancheyta 2013; Ancheyta et al. 2005; Balasubramanian and Pushpavanam 2008; Elizalde et al. 2009; Galarraga et al. 2012; Hassanzadeh and Abedi 2010; Moghadassi et al. 2011).

Models based on pseudocomponents (up to 10) are commonly reported in the literature to simplify the large number of hydrocarbons present in heavy crude oil fractions for lumping purposes during hydrocracking. These models are used to simulate the yield of fractions of interest for refiners or process designers in spite of the reduced amount of information obtained from pseudocomponent-based models. When a distillation curve is required, a small number of pseudocomponents must be interpolated, while the number of kinetic parameters to be calculated increases exponentially, which clearly is not feasible when modeling (Asaee et al. 2014; Becker et al. 2016; Quitian and Ancheyta 2016a; Sadighi et al. 2010).

1.2.1.2 Continuous Lumping Kinetic Models

Continuous models overcome limitations in lumping models by considering that petroleum is formed by an infinite number of components, allowing crude to be considered as a continuous mixture instead of pseudocomponents. Continuous mixing takes into account a large number of undefined species contained in the oil fraction, and the difference between adjacent species is relatively smaller (Ancheyta 2013; Elizalde et al. 2009).

A continuous function describes the reactivity, while the distillation curve is considered to solve the model keeping the number of parameters constant. In addition, properties, such as the carbon number or the true boiling points in distillation, are used to characterize the feedstock and products in the continuous kinetic modeling. The combination of continuous models and pseudocomponents allows more than one continuous distribution to be obtained. However, this model is highly depending on feed properties, and its advantages are as follows (Ancheyta 2013; Becker et al. 2016):

- ✓ Prediction of the distillation curve with few parameters to be estimated
- ✓ Track the chemistry of the process accurately
- ✓ Individual reaction order has physical meaning
- ✓ The properties of fractions between the initial and final boiling points are easily obtained
- ✓ The heteroatom distribution curve is well predicted
- ✓ Easy to adapt to heavy, extra-heavy crudes and residue kinetics

The model involves the dimensionless temperature (θ) and weight fraction, which is calculated as follows:

$$\theta = \frac{\text{TBP} - \text{TBP(l)}}{\text{TBP(h)} - \text{TBP(l)}} \tag{1.1}$$

where TBP is the true boiling point temperature (in kelvin) of any component, TBP(h) and TBP(l) are the highest and lowest boiling points in the mixture, respectively. Because the TBP of the distillation curve is a function of the reactivity (λ), a coordinate transformation between discrete and continuous forms (from the TBP to reactivity for any mixture) is expressed as follows:

$$\frac{\lambda}{\lambda_{\max}} = \theta^{1/\alpha} \tag{1.2}$$

where $\lambda_{\max}$ and α are positive constants and model parameters; $\lambda_{\max}$ is the reactivity for species with the highest dimensionless temperature. The distribution function of species type ($D(\lambda)$) is necessary to transform the coordinates adequately from θ to λ, and it is defined as follows:

$$D(\lambda) = \frac{n_s \alpha}{\lambda_{\max}^{\alpha}} \lambda^{\alpha - 1} \tag{1.3}$$

where n_s is the total number of species in the mixture. The equation of mass balance as a function of the reactivity and residence time (t or LHSV^{-1}) after changing the coordinates, becomes

$$\frac{dc(\lambda, t)}{dt} = -\lambda c(\lambda, t) + \int_{\lambda}^{\lambda_{\max}} p(\lambda, \Lambda) \Lambda c(\Lambda, t) D(\Lambda) d\Lambda \tag{1.4}$$

where $c(\lambda, t)$ is the concentration of the component with reactivity λ, $c(\Lambda, t)$ is the concentration of the component with reactivity Λ, $p(\lambda, \Lambda)$ is the probability density function of species with reactivity Λ that can form species with reactivity λ, Λ is the maximum reactivity of the same component with reactivity λ, and $D(\Lambda)$ is the Jacobian that transforms the discrete coordinate i into a continuous coordinate Λ. The form of the function $p(\lambda, \Lambda)$ and its parameters are given by:

$$p(\lambda, \Lambda) = \frac{1}{S_0 \sqrt{2\pi}} \left[e^{-\left(\left\{ \left[\frac{\lambda}{\Lambda} \right]^{a_0} - 0.5 \right\} \Big/ a_1 \right)^2} - A_1 + B_1 \right] \tag{1.5}$$

$$A_1 = e^{-\left(0.5 / a_1 \right)^2} \tag{1.6}$$

$$B_1 = \sigma \left[1 - \left(\frac{\lambda}{\Lambda} \right) \right] \tag{1.7}$$

where a_0, a_1, and σ are parameters of the model, and S_0 is obtained from the following mass balance criteria:

$$\int_0^{\Lambda} p(\lambda, \Lambda) D(\lambda) d\lambda = 1 \tag{1.8}$$

where $D(\lambda)$ is the Jacobian that transforms the discrete coordinate i into the continuous coordinate λ. Using this equation and solving Eq. (1.5) to S_0, the following solution is reached:

$$S_0 = \int_0^{\Lambda} \frac{1}{\sqrt{2\pi}} \left[e^{-\left(\left\{ \left[\frac{\lambda}{\Lambda} \right]^{a_0} - 0.5 \right\} \Big/ a_1 \right)^2} - A_1 + B_1 \right] D(\lambda) d\lambda \tag{1.9}$$

The hydrocracking phenomena occurring within the reactor are described by the differential equation, which illustrates the formation of compounds resulting from the cracking of components with higher boiling points (second term on the right side of the equation) and the cracking of lower boiling products (first term of the equation). This equation is solved for any residence time in terms of $c(\lambda, t)$, and the desired cuts in mass fraction depending on its dimensionless temperature as follows:

$$C_{\theta_1,\theta_2}(t) = \int_{\lambda_1}^{\lambda_2} c(\lambda, t) D(\lambda) d\lambda \tag{1.10}$$

where $C_{\theta_1,\theta_2}(t)$ is the mass fraction with dimensionless temperature ranging from θ_1 to θ_2 with its corresponding reactivity λ_1 and λ_2 as shown in Eq. (1.2) (Ancheyta 2013; Becker et al. 2016; Elizalde et al. 2009, 2016; Elizalde and Ancheyta 2014; Laxminarasimhan et al. 1996; Martínez-Grimaldo et al. 2011).

1.2.1.3 Single-Event Kinetic Models

Microkinetic models are developed at a molecular scale considering the chemistry of the reaction system by deriving the kinetic equations for individual molecules. The solution adequately converges in reacting systems that contain a limited number of chemical species. However, the set of equations suggested for intricate systems, such as those represented by heavy crude fractions, presents a challenging task to accomplish. Even modern computational tools are unsatisfactory because the size of the reaction network increases exponentially with the number of carbons (Ancheyta et al. 2005; Becker et al. 2016).

The advancement of these types of models for hydrocracking of heavy crude oils is propelled by the rising availability of experimental data gathered using sophisticated analytical techniques and increasing computational capacities. The microkinetic modeling method (single events) was initially proposed by Froment et al. (Baltanas et al. 1989; Baltanas and Froment 1985; Froment 1987; Hillewaert et al. 1988), and the reaction coefficients were calculated for each individual reaction. Computational regrouping algorithms reduce the size of reaction networks without losing information. These can be applied in various reactions, such as hydrocracking, catalytic reformation, isomerization and alkylation; however, the original regrouping method remains as unsuitable for implementation in huge network of reactions, notwithstanding the current computational capabilities. To find an approach, two alternative methods have been proposed (Becker et al. 2016; Guillaume et al. 2011; Mitsios et al. 2009; Valéry et al. 2007): (i) a method based on decomposition of side chains that was developed by Valéry et al. (2007) and (ii) a method based on structural classes, which was developed by Martens and Marin (2001).

1.2.2 Kinetic Models Reported in the Literature for Hydrocracking of Heavy Crude Oils Using Dispersed Catalysts

1.2.2.1 Kinetic Models Based on Distillation Curves

Hassanzadeh and Abedi (2010) as well as Galarraga et al. (2012) carried out experiments for the catalytic heavy crude oil upgrading with dispersed NiWMo catalyst and Athabasca bitumen (9.5 °API) as feed in a batch reactor. The tests were performed at temperature ranges of 320–380 °C, 3–70 h of reaction time, total hydrogen pressure of 3.45 MPa, and stirring rate of 500 rpm. Both works used the same kinetic model (Figure 1.5a) that was first reported by Sánchez et al. (2005a) based on boiling point intervals. The reaction scheme takes into account five lumps: Residue (R, 538 °C+), VGO (343–538 °C), distillates (D, 204–343 °C), naphtha (N, IBP-204 °C), and

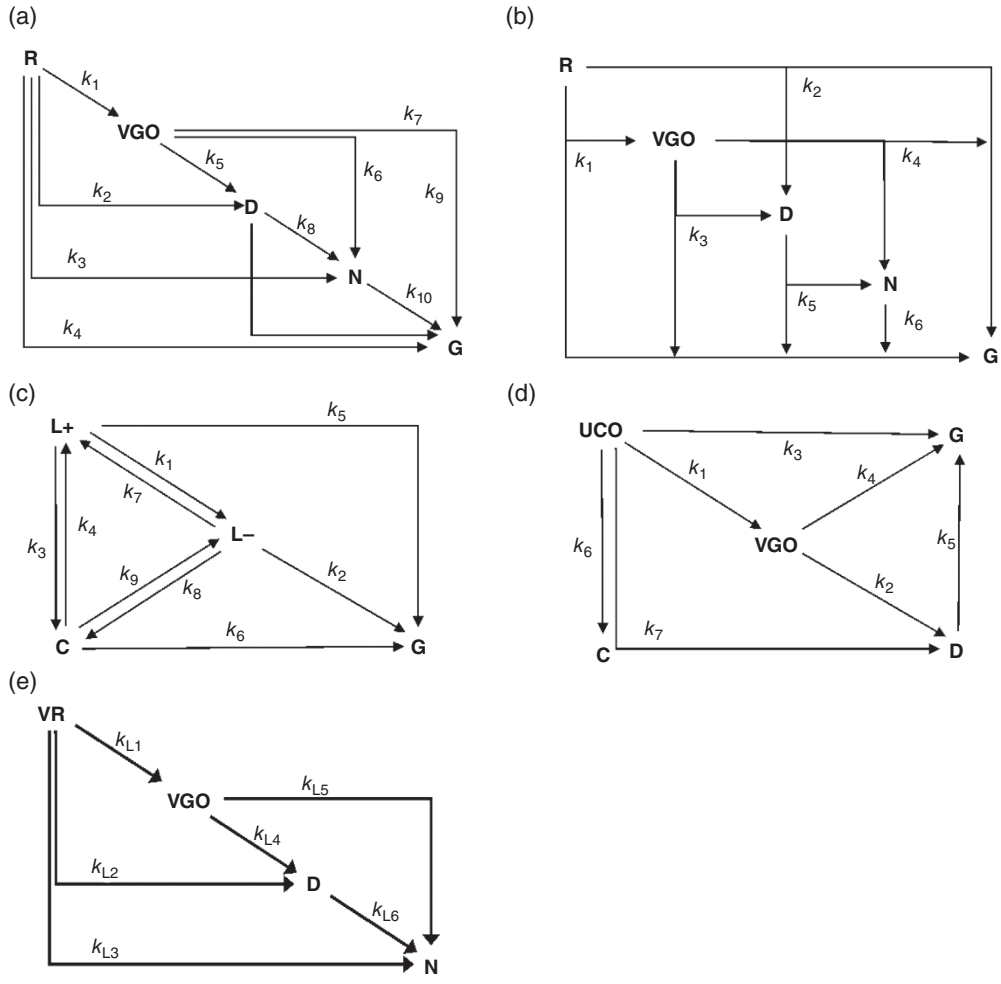

Figure 1.5 Four- and five-lump kinetic models based on distillation curves reported in the literature for heavy oil hydrocracking using dispersed catalyst.

gases (G). Nonetheless, some pseudocomponents proposed by Galarraga et al. (2012) have different boiling point ranges: residue (545 °C+), VGO (343–545 °C), D (216–343 °C), N (IBP–216 °C). The mass balance equations are the same in both cases, and a first-order reaction was considered giving the following expressions:

$$r_R = -(k_1 + k_2 + k_3 + k_4)y_R \tag{1.11}$$

$$r_{VGO} = k_1 y_R - (k_5 + k_6 + k_7)y_{VGO} \tag{1.12}$$

$$r_D = k_2 y_R + k_5 y_{VGO} - (k_8 + k_9)y_D \tag{1.13}$$

$$r_N = k_3 y_R + k_6 y_{VGO} + k_8 y_D - k_{10} y_N \tag{1.14}$$

$$r_G = k_4 y_R + k_7 y_{VGO} + k_9 y_D + k_{10} y_N \tag{1.15}$$

where r_i is the reaction rate of the component i, y_i the mass fractions of component i, k_j the reaction rate coefficients for each reaction pathway j. The only difference is that Hassanzadeh and Abedi

(2010) used the weight fraction, while Galarraga et al. (2012) employed a dimensionless concentration (the concentration at any time divided by the initial concentration). Furthermore, the latter authors performed a general reaction for the residue conversion into light products assuming first-order reaction with k_0 as the only reaction rate coefficient as follows:

$$\text{Residue} \xrightarrow{k_0} \text{Products} \tag{1.16}$$

After the catalytic hydrocracking of Athabasca bitumen with ultradispersed catalyst at bench-scale, kinetic studies on a large-scale reactor were developed by Loria et al. (2011) using the same model as Galarraga et al. (2012). The experimental results were obtained in a pilot plant tubular reactor at reaction temperatures of 320–380 °C, residence times (τ, for continuous reactors is assumed to be the ratio of the reactor volume to the volumetric flow rate) of 9–51 h, keeping the total pressure constant (2.76 MPa), and a hydrogen-to-oil ratio of 3509 (scf/bbl). Although the reaction scheme is the same, some boiling point intervals are different: VGO (343–550 °C) and R (550 °C+). Because an ultradispersed catalyst is employed in the study, the internal and external diffusion and the axial dispersion were negligible in a continuous gas-oil hydrocracking reactor, which allowed to set the reaction equations as follows:

$$\int_{y(\tau_0)}^{y(\tau_f)} dy_{\mathrm{R}} = -k_1\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau - k_2\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau - k_3\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau - k_4\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau \tag{1.17}$$

$$\int_{y(\tau_0)}^{y(\tau_f)} dy_{\mathrm{VGO}} = k_1\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau - k_5\int_{\tau_0}^{\tau_f} yd\tau - k_6\int_{\tau_0}^{\tau_f} y_{\mathrm{VGO}}d\tau - k_7\int_{\tau_0}^{\tau_f} y_{\mathrm{VGO}}d\tau \tag{1.18}$$

$$\int_{y(\tau_0)}^{y(\tau_f)} dy_{\mathrm{D}} = k_2\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau + k_5\int_{\tau_0}^{\tau_f} y_{\mathrm{VGO}}d\tau - k_8\int_{\tau_0}^{\tau_f} y_{\mathrm{D}}d\tau - k_9\int_{\tau_0}^{\tau_f} y_{\mathrm{D}}d\tau \tag{1.19}$$

$$\int_{y(\tau_0)}^{y(\tau_f)} dy_{\mathrm{N}} = k_3\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau + k_6\int_{\tau_0}^{\tau_f} y_{\mathrm{VGO}}d\tau + k_8\int_{\tau_0}^{\tau_f} y_{\mathrm{D}}d\tau - k_{10}\int_{\tau_0}^{\tau_f} y_{\mathrm{N}}d\tau \tag{1.20}$$

$$\int_{y(\tau_0)}^{y(\tau_f)} dy_{\mathrm{G}} = k_4\int_{\tau_0}^{\tau_f} y_{\mathrm{R}}d\tau + k_7\int_{\tau_0}^{\tau_f} y_{\mathrm{VGO}}d\tau + k_9\int_{\tau_0}^{\tau_f} y_{\mathrm{D}}d\tau + k_{10}\int_{\tau_0}^{\tau_f} y_{\mathrm{N}}d\tau \tag{1.21}$$

where τ_0 and τ_f are the initial and final residence times, respectively, and $y(\tau_0)$ and $y(\tau_f)$ are the initial and final weight percentages, respectively, as a function of the residence time.

Nguyen et al. (2013) carried out a kinetic study for the hydrocracking of the Arabian light atmospheric residue in a batch reactor using Mo-dispersed catalyst (molybdenum naphthenate). The experiments were carried out at temperatures of 420–430 °C, residence times of 0.5–1 h, and hydrogen pressure of 15.2 MPa. The proposed reaction scheme (Figure 1.5b) considered the following boiling point intervals: R (510 °C+), VGO (350–510 °C), D (180–350 °C), and N (IBP–180 °C). A first order was assumed for all the reactions and the reaction from R to N was neglected;