



UNIVERSIDAD NACIONAL DE COLOMBIA

# Kinetic mechanism for the cracking of Colombian heavy crude oil fractions in refinery equipments

Luis Carlos López Pérez

Universidad Nacional de Colombia  
Facultad de Minas, Departamento de Procesos y Energía  
Medellín, Colombia

2015

# Kinetic mechanism for the cracking of Colombian heavy crude oil fractions in refinery equipments

Luis Carlos López Pérez

Thesis presented as a partial requirement to obtain the degree of:  
**M.Sc. in Chemical Engineering**

**ADVISOR:**

Alejandro Molina

**RESEARCH GROUP:**

Bioprocesos y Flujos reactivos

Universidad Nacional de Colombia  
Facultad de Minas, Departamento de Procesos y Energía  
Medellín, Colombia  
2015

**Luis Carlos Lopez Perez**

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Master of Science in Chemical Engineering.

---

**(Alejandro Molina) Principal Advisor**

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Master of Science in Chemical Engineering.

---

**(Hugo De Lasa) Evaluator**

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Master of Science in Chemical Engineering.

---

**(Astrid Sanchez) Evaluator**

# Dedication

*To my parents. To my brother and sisters.*

*«Until the day when God shall deigns to reveal the future to man, all human wisdom is summed up in these two words: wait and hope.» **Edmond Dantes***

# ACKNOWLEDGEMENTS

Al apoyo incondicional de mis padres, Marcelino y María Eugenia, y a mis hermanos Jose y Ceci, que siempre me han acompañado y apoyado en todo momento.

Al profesor Alejandro Molina por su apoyo moral, sobre todo por su paciencia y por compartir su experiencia y conocimientos para llevar a cabo este trabajo. Sin su ayuda esto no hubiese sido posible. Gracias infinitas para darme la oportunidad de hacer parte de este proyecto y de su grupo de investigación.

Al Instituto Colombiano del Petróleo ICP-Ecopetrol por la financiación de este proyecto en el marco del Convenio de Cooperación Tecnológica No. 003. y a Colciencias y Ecopetrol por la financiación de esta tesis enmarcada en el proyecto "Desarrollo de herramientas de simulación para la refinación de crudos pesados - Aproximación mediante Dinámica de Fluidos Computacional (CFD)".

Al grupo de investigación Bioprocesos y Flujos reactivos por su aportes y comentarios a lo largo de este proceso de investigación. Y obvio, a mi equipo de trabajo, Juanjo, Noel, Sandra, Amérika, Jorge Luis, el Juanda, y David, por sus aportes y su paciencia durante las reuniones.

Agradecimiento especial al profesor Markus Kraft por sus aportes durante los últimos dos meses y por darme la oportunidad de hacer la pasantía en Singapur y ser parte del Cambridge Center for Advanced Research in Energy Efficiencies in Singapore (CARES). De igual forma,

mi mas sincero agradecimiento a aquellos miembros de CARES: Linus, Jannice, Martin, Kevin, que hicieron de mi estadía una mejor experiencia.

«¡GRACIAS TOTALES!» a mis amigos que siempre han estado durante este proceso. En especial al Manco, mi llave. Y a todos los que siempre aportaron de una u otra forma en el desarrollo de esta tesis.

---

# ABSTRACT

We present a methodology for developing lump-mechanisms for the main three refinery processes with heavy crude oil fractions. Hydrocracking, Fluid Catalytic Cracking and Delayed Coking. Given the available resources, Colombia has a strong trend to process heavy crude oil fractions instead of the light ones; thus, through simulation methods, this thesis focus on solving one of problems of heavy crude oil fractions associated with its simulation. It is well known that the heavy crude oil fractions are composed by a large number of species, and therefore, a detailed kinetic mechanism implies the modeling of a large number of reactions. Thus, lump-mechanisms were used to give an approximate representation of the cracking processes in each equipment. The lump-mechanisms were obtained through a regression of experimental data reported for each process. The experimental data collected in literature were standardized in a eXtensible Mark-Up language database to facilitate the reading by the simulation softwares. Initially, we fitted the data to a mechanism reported in literature through an optimization method. We calculated the best set of kinetic parameters using *fmincon* routine available in Matlab 2014. Using a wide range of process conditions from many different experiments instead of one or two experiments provides a global vision about each process. This thesis considered a wide range of operational conditions for each process. For hydrocracking such as: temperature, varying from 360°C to 450°C; Liquid Hourly Space Velocity (LHSV) varying from 0.9 h<sup>-1</sup> to 1.36 h<sup>-1</sup>. This thesis also evaluated a wide range of the other processes, for Fluid Catalytic Cracking included experimental data obtained from experiments carried out in batch reactors and Plug-Flow Reactors (PFR). For delayed coking the operational conditions such as: temperature varying from 410°C to 475°C and residence times varying from 0.5 h<sup>-1</sup> to 3 h<sup>-1</sup>. A regression analysis shows good accuracy between the data predicted by the model and experimental data. The regression coefficients were 0.96, 0.68 and 0.84 for the three processes respectively.

A bootstrap methodology was used to calculate the confidence interval and standard uncertainty for the parameters associated to each process. Bootstrap consisted in a re-sampling with replacement of experimental data vector for each process. Once the re-sampled vector is generated, the optimization was carried out to get the set of kinetic parameters. Therefore, independent samples were obtained. The process is repeated 2000 times to create a big sample of the kinetic parameters and therefore calculate the mean value and the standard uncertainty. The results showed values of standard uncertainties around two magnitude or-

ders less than the mean value of the distribution. Kinetic results showed the compensation effect for those processes which were modeled using first-order and irreversible reactions such as hydrocracking and delayed coking. For each kinetic parameter, a sensitivity analysis was carried out to determine the success of the optimization routine and to determine the number of bootstrap re-samplings. Results showed that the calculated parameters corresponded to a global minimum in the optimization.

**Keywords:** Bootstrap, Kinetic parameter estimation, Refinery process, Sensitivity analysis, Uncertainty calculation.



---

## RESUMEN

Se desarrolló una metodología para desarrollar mecanismos tipo lumps para tres de los mas importantes procesos que operan con fracciones de crudo pesado en refinería. Debido a la tendencia en Colombia a procesar crudos pesados y fracciones pesados de petróleo, esta tesis busca solucionar problemas con respecto al modelamiento de fracciones de crudos pesados. Los tres procesos que se van a trabajar en esta tesis son hidrocraqueo, craqueo catalítico y coquizacion retardada. Para cada proceso, se siguió la misma metodología para la obtención de parámetros cinéticos y sus respectivas incertidumbres. Mecanismos tipo lumps fueron utilizados para representar las fracciones mas importantes en cada proceso. Los parámetros cinéticos de estos mecanismos se obtuvieron mediante una regresion teniendo en cuenta la mayor cantidad de datos tomados de literatura para cada proceso. Los datos experimentales se almacenaron en una base de datos en formato XML (eXtensible Mark-Up Language) que implica una lectura más fácil desde cualquier software de simulación. Los mecanismos para cada proceso se tomaron despues de un análisis de literatura y determinar que la cantidad de lumps fueran suficientes para predecir los productos mas importantes en cada proceso. Así, despues de definir el mecanismo y los parámetros cinéticos, se realizó una optimización en Matlab 2014, se utilizo la rutina *fmincon* para calcular el mejor conjunto de parametros cinéticos que permitan un buen ajuste del modelo con respecto a los datos tomados de literatura. Un amplio rango de condiciones de operación para cada proceso se tuvieron en cuenta durante la optimización. Para el caso del mecanismo de hidrocraqueo, este consideró temperaturas entre 360°C y 450°C y tiempos de residencia desde 0.9 h<sup>-1</sup> hasta 1.36 h<sup>-1</sup>. De igual forma, para los otros procesos también se consideraron diferentes condiciones de operación para garantizar un rango de operación mayor para el mecanismo. Para el caso de craqueo catalítico, se consideraron datos experimentales obtenidos en reactores tipo batch y reactores riser. Mientras que para la coquización retardada, se consideraron intervalos de temperatura entre 410°C y 475°C y tiempos de residencia entre 0.5 h<sup>-1</sup> hasta 3 h<sup>-1</sup>. El uso de un amplio rango en las condiciones de operación del proceso debido a los datos experimentales que se recolectaron para la optimización permite una vision global y un mejor entendimiento del proceso. Finalmente, un análisis de regresión mostró un buen desempeño entre los datos predichos por el modelo y los datos experimentales regresión para cada mecanismo. Los coeficientes de regresión para cada proceso fueron 0.96, 0.68 and 0.84 respectivamente.

Por último, se utilizó la tecnica bootstrapp para calcular los intervalos de confianza y las in-

certidumbres estándar para los parámetros correspondientes a cada mecanismo. Esta técnica consistió en hacer un remuestreo con reemplazo del vector de datos experimentales para cada proceso. Por cada remuestreo, se realizó una optimización para obtener un conjunto de parámetros cinéticos. En total, se hicieron 2000 remuestreos y así crear una muestra cuyos valores son los parámetros cinéticos independientes entre sí. De esta forma se calcularon la media de cada muestra y su incertidumbre estándar. Los resultados mostraron valores de incertidumbre hasta dos órdenes de magnitud menor a los valores de los parámetros cinéticos. Además, los resultados cinéticos mostraron el efecto compensatorio para cada par de parámetros cinéticos correspondientes a la misma reacción para aquellos procesos que se modelaron utilizando cinéticas de primer orden y reacciones irreversibles tales como el hidrocrackeo y la coquización retardada. Para cada parámetro cinético, se realizaron análisis de sensibilidad, uno para determinar si la optimización convergió a un mínimo global y el segundo para determinar el número necesario de remuestreos en la técnica bootstrap. Los resultados una vez más mostraron que los parámetros que se obtuvieron para cada mecanismo correspondían a un mínimo global y además se determinó el número de iteraciones suficientes de remuestreo.

**Palabras clave:** Cálculo de incertidumbres, procesos de refinería, bootstrap, estimación de parámetros cinéticos, análisis de sensibilidad.

# CONTENTS

<b>Acknowledgements</b>	<b>v</b>
<b>ABSTRACT</b>	<b>vii</b>
<b>RESUMEN</b>	<b>ix</b>
<b>List of Tables</b>	<b>xiii</b>
<b>List of Figures</b>	<b>xiv</b>
<b>1. Introduction</b>	<b>2</b>
1.1. Objectives . . . . .	5
1.1.1. Overall Objective . . . . .	5
1.1.2. Specific Objectives . . . . .	5
<b>2. Literature review</b>	<b>6</b>
2.1. Hydrocracking . . . . .	6
2.1.1. Process description . . . . .	6
2.1.2. Kinetic mechanisms . . . . .	8
2.1.3. Hydrocracking mechanisms Summary . . . . .	10
2.2. Fluid catalytic cracking . . . . .	13
2.2.1. Process description . . . . .	13
2.2.2. kinetic mechanisms . . . . .	15
2.3. Delayed coking . . . . .	25
2.3.1. Process description . . . . .	25
2.3.2. Kinetic mechanisms . . . . .	26

---

<b>3. Methodology</b>	<b>32</b>
3.1. Catalytic Hydrocracking . . . . .	32
3.1.1. XML (eXtensible Mark-Up Language) data standardization . . . . .	32
3.1.2. Lumps selection . . . . .	33
3.1.3. Modeling and equations . . . . .	34
3.1.4. Kinetic Parameter Estimation . . . . .	36
3.1.5. Uncertainty Calculation . . . . .	39
3.2. Fluid Catalytic Cracking (FCC) . . . . .	42
3.2.1. XML (eXtensible Mark-Up Language) data standardization . . . . .	42
3.2.2. Lumps selection . . . . .	44
3.2.3. Modeling and equations . . . . .	45
3.2.4. Kinetic Parameter Estimation . . . . .	47
3.3. Delayed Coking Process . . . . .	48
3.3.1. XML (eXtensible Mark-Up Language) data standardization . . . . .	48
3.3.2. Modeling and equations . . . . .	49
3.3.3. Kinetic Parameter Estimation . . . . .	50
<b>4. Results and Analysis</b>	<b>51</b>
4.1. Hydrocracking . . . . .	51
4.1.1. Data compilation . . . . .	51
4.1.2. Optimization and uncertainty calculation . . . . .	52
4.2. Fluid Catalytic Cracking . . . . .	59
4.2.1. Data compilation . . . . .	59
4.2.2. Optimization and uncertainty calculation . . . . .	59
4.3. Delayed Coking . . . . .	67
4.3.1. Data compilation . . . . .	67
4.3.2. Optimization and uncertainty calculation . . . . .	67
<b>5. Conclusions</b>	<b>72</b>
<b>A. Main statistical properties for Hydrocracking</b>	<b>74</b>
<b>B. Main statistical properties for Fluid Catalytic Cracking</b>	<b>81</b>
<b>C. Main statistical properties for Delayed Coking</b>	<b>89</b>
<b>D. Differences between the type of Arrhenius equation in the Sensitivity Analysis</b>	<b>95</b>

<b>E. XML data base for HC, FCC and DC</b>	<b>97</b>
<b>References</b>	<b>154</b>

# List of Tables

<b>2-1.</b> List of lump-mechanisms reported in the HC literature . . . . .	9
<b>2-2.</b> List of lump-mechanisms reported in the HC literature . . . . .	10
<b>2-3.</b> Summary of HC mechanisms . . . . .	11
<b>2-5.</b> Summary of HC mechanisms . . . . .	12
<b>2-7.</b> Ten-lump mechanism proposed by Jacob et al. [1] . . . . .	17
<b>2-8.</b> Eleven-lump mechanism proposed by Barbosa et al. [2] . . . . .	18
<b>2-9.</b> Summary of FCC mechanisms . . . . .	21
<b>2-11.</b> Summary of FCC mechanisms . . . . .	22
<b>3-1.</b> Range for each process conditions for the FCC . . . . .	43
<b>3-2.</b> Summary of process conditions stored in the XML database for Fluid Catalytic Cracking . . . . .	44
<b>4-1.</b> Uncertainty values for each kinetic parameter obtained from the bootstrap technique . . . . .	53
<b>4-2.</b> Uncertainty values for each kinetic parameter obtained from the bootstrap technique for the proposed mechanism for FCC . . . . .	61
<b>4-3.</b> Uncertainty values for each kinetic parameter obtained from the bootstrapp technique . . . . .	69

# List of Figures

<b>1-1.</b> Refinery process conceptual scheme . . . . .	3
<b>2-1.</b> Catalytic hydrocracking conceptual scheme . . . . .	7
<b>2-2.</b> Two-lumps hydrocracking mechanism proposed by Qader et al. [3] . . . . .	9
<b>2-3.</b> FCC conceptual scheme . . . . .	14
<b>2-4.</b> Three-lump kinetic mechanism proposed by Weekman et al. 1969 [4] . . . . .	16
<b>2-5.</b> Five-reactions kinetic mechanism proposed by Arbel et al. 1995 [5] . . . . .	24
<b>2-6.</b> Two-reactions kinetic mechanism proposed by Arandes et al. 1999 [6,7] . . . . .	25
<b>2-7.</b> Schematic figure for Delayed Coking process . . . . .	26
<b>2-8.</b> Four-lumps kinetic mechanism proposed by Del Bianco et al. 1993 [8] VR: Vacuum Residue Crude Oil; . . . . .	28
<b>2-9.</b> Four-lumps kinetic mechanism proposed by Sawarkar et al. [9] VR: Vacuum Residue crude oil . . . . .	29
<b>2-10.</b> Six-lumps kinetic mechanism using SARA methodology , proposed by Koseo- glu et al. [10] . . . . .	30
<b>2-11.</b> Seven-lumps kinetic mechanism using SARA methodology , proposed by Filho et al. [11] . . . . .	30
<b>3-1.</b> Tree-like structure used in this thesis for data storage taken from literature for HC. . . . .	34
<b>3-2.</b> Five-lumps hydrocracking mechanism proposed by Martinez and Ancheyta [12] . . . . .	37
<b>3-3.</b> Four-lumps hydrocracking mechanism proposed in this thesis. . . . .	37
<b>3-4.</b> Algorithm that summarize the bootstrapping technique to calculate the un- certainty of the kinetic parameters. . . . .	41
<b>3-5.</b> Tree-like structure used in this thesis for data storage taken from literature for HC. . . . .	43
<b>3-6.</b> Four-lumps FCC mechanism proposed in this thesis. . . . .	45

4-1. Four-lumps HC mechanism proposed in this thesis. . . . .	52
4-2. Parity plot for the model prediction and data taken from literature [13–16]. . . . .	54
4-3. Sensitivity of the objective function to variations in the activation energy of the reaction 1 of the mechanism in Figure 4-1 . . . . .	55
4-4. Comparison between experimental in reference [17] for HC of an oil fraction and the model using the parameters in the Table 4-1. . . . .	56
4-5. Variation of the activation energies with respect to number of bootstrap resampling . . . . .	57
4-6. Variation of the standard deviation of activation energies with respect to number of bootstrap resampling . . . . .	57
4-7. Histogram distribution for the activation energy corresponding to reaction 1 for HC mechanism . . . . .	58
4-8. Scatter distribution for the kinetic parameters for the reactions 3 and 4 . . . . .	59
4-9. Four-lumps FCC mechanism proposed in this thesis. . . . .	60
4-10. Parity plot for the model prediction and data taken from literature [18–25] . . . . .	61
4-11. Sensitivity for activation energy of the reaction 1 of the proposed mechanism for FCC . . . . .	62
4-12. Representation of the experimental data for FCC Industrial riser using the parameters in Table 4-2 . . . . .	63
4-13. Variation of the activation energies with respect to number of bootstrap resampling . . . . .	64
4-14. Variation of the standard deviation for activation energies with respect to number of bootstrap resampling . . . . .	65
4-15. hystogram distribution for kinetic parameter corresponding to reactions 1 and 2 . . . . .	65
4-16. Scatter distribution for the kinetic parameters for the reaction 3 . . . . .	66
4-17. Four-lumps DC mechanism proposed in this thesis. . . . .	67
4-18. Parity plot for the model prediction and data taken from literature. . . . .	68
4-19. Sensitivity for activation energy of the reaction 1 of the proposed mechanism for DC . . . . .	69
4-20. Histogram distribution for kinetic parameter corresponding to reaction 1 . . . . .	70
4-21. Variation of the activation energies with respect to number of bootstrap resampling . . . . .	71
4-22. Scatter distribution for the kinetic parameters for DC for the reaction 1 . . . . .	71



---

<b>A-1.</b> Sensitivity for activation energy and preexponential factor of the main reactions in HC . . . . .	75
<b>A-2.</b> Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 2 . . . . .	76
<b>A-3.</b> Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 3 . . . . .	76
<b>A-4.</b> Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 4 . . . . .	77
<b>A-5.</b> Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 5 . . . . .	77
<b>A-6.</b> Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 6 . . . . .	78
<b>A-7.</b> histograms for the distribution of values for the kinetic parameters corresponding to reaction 2 . . . . .	78
<b>A-8.</b> histograms for the distribution of values for the kinetic parameters corresponding to reaction 3 . . . . .	79
<b>A-9.</b> histograms for the distribution of values for the kinetic parameters corresponding to reaction 4 . . . . .	79
<b>A-10</b> histograms for the distribution of values for the kinetic parameters corresponding to reaction 5 . . . . .	80
<b>A-11</b> histograms for the distribution of values for the kinetic parameters corresponding to reaction 6 . . . . .	80
<b>B-1.</b> Sensitivity for the pre-exponential factor of reaction 1 . . . . .	81
<b>B-2.</b> Sensitivity for the pre-exponential factor of reaction 1 . . . . .	82
<b>B-3.</b> Sensitivity for the pre-exponential factor of reaction 1 . . . . .	83
<b>B-4.</b> Sensitivity for the pre-exponential factor of reaction 1 . . . . .	84
<b>B-5.</b> distribution of kinetic parameters for reaction 1 . . . . .	85
<b>B-6.</b> distribution of kinetic parameters for reaction 2 . . . . .	86
<b>B-7.</b> distribution of kinetic parameters for reaction 3 . . . . .	87
<b>B-8.</b> distribution of kinetic parameters for reaction 4 . . . . .	88
<b>C-1.</b> Sensitivity analysis for kinetic parameters corresponding to reaction 1 . . . .	89
<b>C-2.</b> Sensitivity analysis for kinetic parameters corresponding to reaction 2 . . . .	90
<b>C-3.</b> Sensitivity analysis for kinetic parameters corresponding to reaction 3 . . . .	91
<b>C-4.</b> distribution of kinetic parameters for reaction 1 . . . . .	92

---

<b>C-5.</b> distribution of kinetic parameters for reaction 2 . . . . .	93
<b>C-6.</b> distribution of kinetic parameters for reaction 3 . . . . .	94
<b>D-1.</b> value of the objective function when use both Arrhenius equation. Red line: Eq. number 1. Blue line: Eq. number 2 . . . . .	96

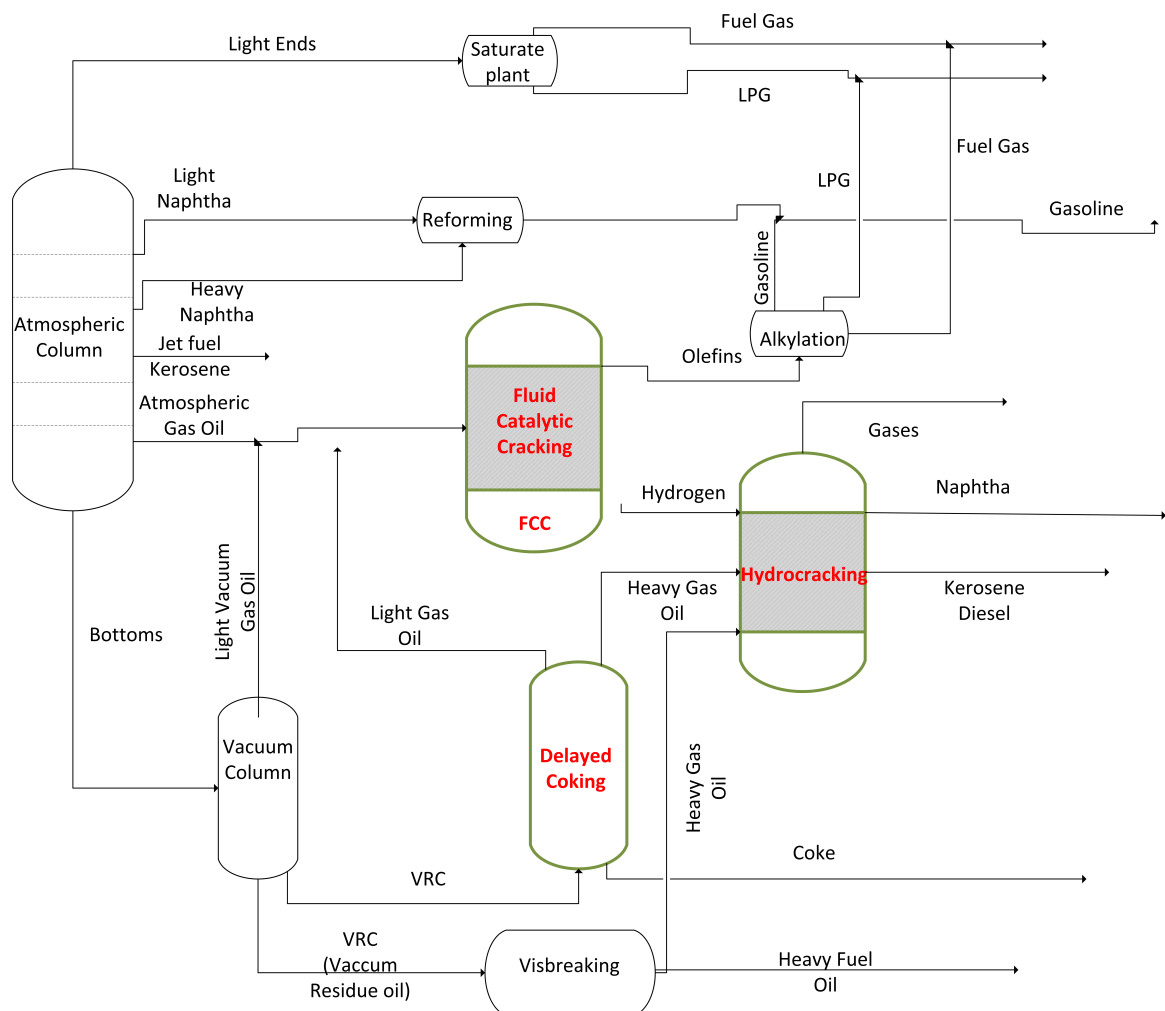
# 1. Introduction

Decreasing stock of light oil in some countries, such as Colombia, has forced the use of heavier oils. The change to heavier raw material demands the understanding of the behavior of heavy crude oil fractions during the thermal decomposition. In this process coke formation is unavoidable, mainly due to higher quantity of asphaltenes in the heavy crude oil fractions, higher temperatures inside the cracking equipment and longer residence times in the processes. A better understanding of the phenomena involved in oil cracking can help to solve or avoid possible problems in the operation of heavy-oil upgrading equipment.

Currently, the most inefficient processes for the transformation of heavy crude oil fractions are: Hydrocracking (HC), Fluid Catalytic Cracking (FCC), and Delayed Coking (DC). Figure **1-1** shows a diagram of a typical refinery. Atmospheric column converts crude oil into light ones such as naphthas, kerosene and gasoline. The residue goes to a vacuum distillation unit where it is separated into Vacuum Gas Oil (VGO) which constitute the main feedstock for FCC and HC to produce light products, and Vacuum Residue Oil (VRC) which is fed to the DC to produce coke and VGO .

Simulation tools such as Computational Fluid Dynamics (CFD) play an important role in the simulation of these processes. Several studies to improve the performance of refinery equipment have been developed [2,20,26]. CFD tool is one of the most practical techniques to make fast changes in the geometry and process conditions of refinery equipment. The three main steps required to carry out a CFD simulation of a reacting system are: a) discretization and meshing of the control volume; b) solution of the mass, momentum, species and energy equations and a; c) kinetic mechanisms. This thesis focuses in CFD simulation, but, in how to develop properly a kinetic mechanism suitable for CFD simulations.

Despite being a powerful tool in process modeling, CFD has limitations with the simulation of complex kinetic mechanism mainly because the high computational cost that one would expect highly improbable to conduct a CFD simulation. Given the complex of the



**Figure 1-1.** Refinery process conceptual scheme

composition of heavy crude oil fractions that comprises hundreds and even thousands of reactions, several techniques have been developed to represent the large number of species and reactions as a reduced number of pseudo-components selected based on their similarities in physical properties such as boiling point, density, molecular structure, among others.

A lumping technique is one of the ways to represent a large and complex reaction model containing a large number of reactive components. Lumping is based on the reduction of the number of the mixture into a lower number of representative components still able to describe the behavior of the original mixture. The lumping technique has some limitations such as the low-level of detail of the chemistry that it gives. This technique have been widely used in literature to represent the refinery processes [1, 12, 27].

Usually the development of a kinetic mechanism for CFD simulations follows two approaches; one case, the most widely used validates the data with experiments carried out by the same research team carrying out the experiments. This way to get kinetic mechanisms, is the most desirable because it guarantees kinetic parameters obtained at the operational conditions of the actual process and enables a better quantification of uncertainty values. However, this tool is not always available due to limitations in infrastructure or budget.

Usually, the alternative when experiments are not affordable is to select one mechanism from the open literature. This is clearly a less expensive and simpler approach and could yield good results when the process to be simulated is at similar conditions to those used to infer the kinetic parameters. A mechanism taken from literature, however, could lead to loss of information and have limited application for a feedstock different from that used in the experiments.

This thesis gives another perspective to kinetic parameter estimation when a set of experiments is not available. The main contribution of this alternative is to take as much as possible data from literature, and build a standard database using the XML language. Unlike previous researches that only considered one reference, or in the best case, has experimental data for validation, this alternative enables a global perspective about the process and it could be extended the range of process conditions.

This thesis is organized as follows: Chapter 2 gives a background on the refinery processes mentioned above: HC, FCC and DC. The chapter ends with a detailed review of the literature available on kinetic mechanisms for each process. Chapter 3 describes the methodology for developing the kinetic lump-mechanism from experimental data available in the open literature. This methodology describes mathematical and statistical tools and also the software and algorithms used to determine the kinetic parameter values and its respective uncertainties. Chapter 4 presents as main result of this study the lump-mechanism for each process. Finally, Chapter 5 shows the main conclusions and contributions of this thesis.

## **1.1. Objectives**

### **1.1.1. Overall Objective**

To develop a kinetic mechanism to represent the cracking of Colombian heavy crude oil in delayed coking, fluid catalytic cracking and hydrocracking units.

### **1.1.2. Specific Objectives**

1. To evaluate the behavior of kinetic mechanisms available on literature to predict the thermal cracking in refineries.
2. To propose a kinetic mechanism to predict the cracking of a Colombian heavy crude oil for the selected refinery equipments using statistical tools.
3. To validate the kinetic mechanism with experimental data available on literature and industrial data.

## 2. Literature review

This chapter describes of the three refining processes that are the subject of this study: Hydrocracking (HC), Fluid Catalytic Cracking (FCC) and Delayed Coking (DC). The chapter also describes the kinetic mechanisms that have been proposed along the years for these three processes and their main differences, according to the number of lumps and the experimental operational conditions at which they were obtained. At the end of the description of each process, a table summarizes all the kinetic mechanisms treated in this thesis.

### 2.1. Hydrocracking

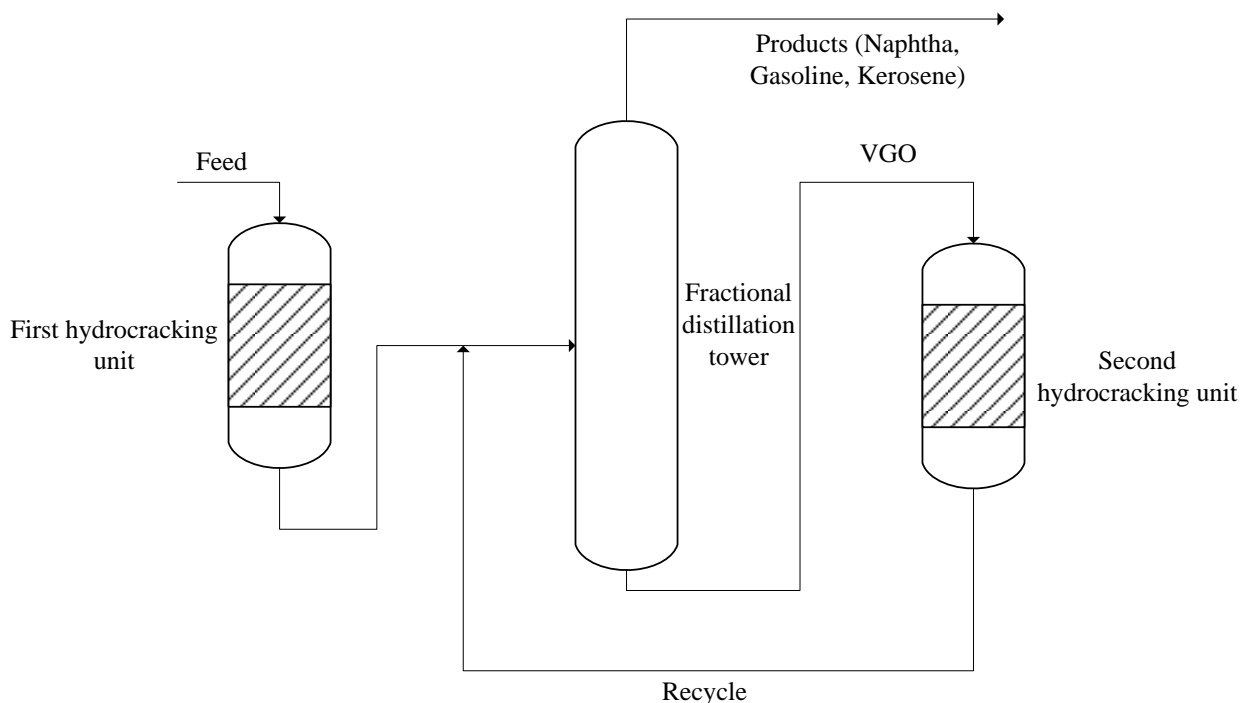
#### 2.1.1. Process description

Catalytic hydrocracking is widely used in refineries for the upgrading of Vacuum Gas Oil (VGO) from vacuum or atmospheric distillation units. HC produces low molecular weight compounds through thermal cracking reactions carried out on a catalytic surface and under a hydrogen-rich atmosphere. Also, in this process, hydrotreatment reactions such as hydrodesulfuration and hydrodenitrogenation take place.

Figure **2-1** describes the two-step hydroprocessing of a heavy crude oil fraction. The feed consists mainly by hydrogen and the heavy crude oil fraction, in this case VGO with a high concentration of sulfur and nitrogenated compounds. The feed enter to the first HC unit, where hydrocracking and hydrotreatment reactions take place. The first step uses a non-selective catalyst to remove the heavier compounds such as metals and sulfur from the VGO. This helps to obtain a better upgrade in the next step.

The stream from the first unit goes to the fractional distillation tower, which separates the stream from the first unit and from the recycle to produce an upgraded VGO (VGO

stream in Figure 2-1), which goes to the second hydrocracking unit. The second unit, uses a selective catalyst such as Alumina or Ni-Mo to further upgrade the oil fraction. The light compounds such as naphthas, gasoline and kerosene are recirculated and finally separated in the fractional distillation tower.



**Figure 2-1.** Catalytic hydrocracking conceptual scheme

The petrochemical industry typically prefers to conduct HC in two kinds of reactors: fixed trickle bed reactor (TBR) and ebullated bed reactor (EBR). Although in both reactors three phases (oil, catalyst and hydrogen) coexist, the industry prefers TBR because it works in down flow mode, with a liquid and gas phase on the catalytic bed. In this process, the catalyst stimulates coke deposition which produce a fouling of catalyst, which could occur when VGO conversion is greater than 50 %.

HC produces light-weight and high-commercial value products which are characterized according to its boiling point. The products are gases ( $0^{\circ}\text{C}$ - $32^{\circ}\text{C}$ ), naphthas between  $\text{C}_5$ – $\text{C}_{14}$  ( $32^{\circ}\text{C}$ - $150^{\circ}\text{C}$ ), gasoline and kerosene ( $150^{\circ}\text{C}$  -  $343^{\circ}\text{C}$ ), and in most of the cases, residual VGO ( $343^{\circ}\text{C}$ ) due to an intentional incomplete conversion to avoid coke formation in the catalyst, which implies high regeneration costs.



### 2.1.2. Kinetic mechanisms

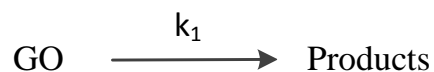
The complexity of the chemical reactions that take place in the HC reactor, and the complex characterization of heavy residue, could be a problem when developing a kinetic mechanism to represent this process. The representation of these hydrocarbons mixtures through *Lumping* methodology enables to group these species into a smaller number of pseudocomponents according to similarities in physical and chemical properties such as boiling point, adsorption and solubility. In most cases the *Lumping* methodology groups the compounds through boiling points.

Lump-mechanisms have been widely used to describes the HC. Qader et al. [3] in 1969 conducted experiments for the study of HC of gas oil, They carried out the experiments in a Packed Bed Reactor (PBR) and determined first-order reaction kinetics for the HC of gas oil. They proposed a two-lumps mechanism as shown in Figure 2-2, that included the kinetic parameters in a typical temperature range (400°C-500°C) for a space velocity between 0.5 h<sup>-1</sup> and 3 h<sup>-1</sup>. The mechanism in Figure 2-2 represents the most important compounds obtained in the hydrocracking process with a very simplified approach that grouped all products in one pseudocomponent called "PRODUCTS". The authors also concluded that conversion to gasoline increases when temperature decreases and space time increases. The authors obtained the highest conversion at 500°C and 0.5 h<sup>-1</sup> of space velocity at pressure of 10.3 MPa.

Later studies considered *Lumping* methodology as a way for developing of kinetic mechanisms. Thus, some lump-mechanisms were proposed [12–15, 28–34] to describes the HC process under its typical operational conditions. More recent studies involved lump-mechanisms with a higher number of lumps and reactions as the mechanisms proposed by Asaee et al. [35] that involves a complex hydroconversion for a VRC including hydrocracking of VGO and another upgrading processes.

Despite of the differences between the mechanisms such as the number of the lumps, these experiments were conducted in a range of temperature from 350°C to 450°C, 0.5 h<sup>-1</sup> and 2 h<sup>-1</sup> of LHSV and a pressure between 5 MPa to 14 MPa.

A list of lump-mechanisms for HC is presented in Table 2-1. The table shows the evolution of the lump-mechanisms along the years and we can conclude that there is a trend in the increasing the number of lumps and reactions in more recent studies in order to give a more detailed about the process given that the evolution of the computational tools.



**Figure 2-2.** Two-lumps hydrocracking mechanism proposed by Qader et al. [3]

**Table 2-1.** List of lump-mechanisms reported in the HC literature

Author	Number of lumps	Number of reactions	Year
Qader et al. [3]	2	1	1969
Orochko et al. [28]	3	3	1970
Aboul-Geit et al. [13]	4	3	1989
Yui and Sandford et al. [29]	4	3	1989
Callejas and Martinez. [30]	2	2	1997
Aoyagi et al. [31]	3	3	2003
Botchwey et al. [32]	4	5	2003
Botchwey et al. [15]	6	8	2004
Sánchez et al. [33]	5	10	2005
Valavarasu et al. [34]	4	6	2007
Sadighi et al. [14]	4	6	2010
Martinez et al. [12]	5	10	2012
Asaee et al. [35]	6	12	2014

As it was mentioned in the Chapter 1, the differences in the VGO in each experiment for HC leads to the last authors to get different results despite to develop their experiments under

similar operational conditions, hence, it would expect that kinetic parameters obtained for each proposed HC lump-mechanism were different, as shown in Table **2-2**

**Table 2-2.** List of lump-mechanisms reported in the HC literature

Reactions	Reported Activation energies (kJ/mol)						
	Ref. [33]	Ref. [12]	Ref. [34]	Ref. [29]	Ref. [28]	Ref. [30]	Ref. [13]
$R \rightarrow VGO$	203.1	136.0	-	-	-	-	-
$R \rightarrow MD$	185.1	167.0	-	-	-	-	-
$R \rightarrow Naphtha$	159.1	192.0	-	-	-	-	-
$R \rightarrow Gas$	114.3	261.0	-	-	-	-	-
$VGO \rightarrow MD$	165.4	145.0	164.8	59.9	-	269.5	73.3
$VGO \rightarrow Naphtha$	155.3	190.0	241.8	234.7	-	-	100.5
$VGO \rightarrow Gas$	-	-	207.5	-	-	294.9	78.2
$MD \rightarrow Naphtha$	224.8	146.0	185.4	85.7	-	-	-
$MD \rightarrow Gas$	-	-	192.2	-	-	-	-
$Naphtha \rightarrow Gas$	-	-	48.7	-	-	-	-

The number of lumps and reactions strongly depend the process condition which the experiments were conducted. We can observe in Table **2-2** the differences in the reactions for each lump-mechanism. Some of them [12,30,33] include gas formation, given that their experiments were conducted at temperatures greater than 420°C. Otherwise, those experiments carried out at temperatures less than 420°C did not include the gas formation in their respective mechanism [29].

### 2.1.3. Hydrocracking mechanisms Summary

We present a summary of the main HC mechanisms in (2-3) and (2-5). For each mechanism, the table shows the kinetic model, the feed characteristic, operational conditions for the experiments, and the main conclusions and contributions.

Table 2-3. Summary of HC mechanisms

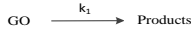
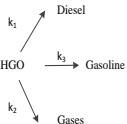
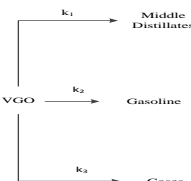
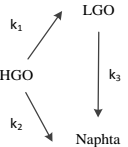

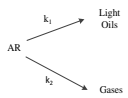
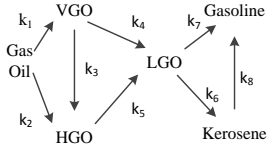
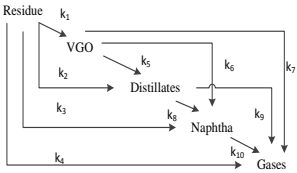
Kinetic model	Authors	Feed Characteristics	Process	S.N	Conclusions
 <p>GO <math>\xrightarrow{k_1}</math> Products</p>	Qader et al [3].	Gas oil with API gravity equal to 31.9° and boiling point range between 300°C y 430°C (573-703 K)	Continuous fixed-bed tubular flow reactor over a ceramic catalytic surface at constant temperature.	1	The overall rates of gas oil hydrocracking can be expressed as simple first-order kinetic equations.
 <p>HGO <math>\xrightarrow{k_1}</math> Diesel  HGO <math>\xrightarrow{k_2}</math> Gasoline  HGO <math>\xrightarrow{k_3}</math> Gases</p>	Orochko et al. [28].	Romashkin and Arlan petroleum vacuum distillates	Hydrocracking of vacuum residues on a alumina-cobalt-molybdenum catalyst.	2	First order reactions for hydrocracking of vacuum residue. The mechanism showed a good agreement with the experimental data.
 <p>VGO <math>\xrightarrow{k_1}</math> Middle Distillates  VGO <math>\xrightarrow{k_2}</math> Gasoline  VGO <math>\xrightarrow{k_3}</math> Gases</p>	Aboul-Gheit [13]	Non specified VGO	VGO hydrocracking using two different catalyst: Two kinds of NiMo with HY Zeolite on a silica-alumina matrix.	3	Authors suggested VGO reacts to form gases, gasoline and middle distillates. First-order rate constants for the hydrocracking reactions.
 <p>HGO <math>\xrightarrow{k_1}</math> LGO  HGO <math>\xrightarrow{k_2}</math> Naphta  LGO <math>\xrightarrow{k_3}</math> Naphta</p>	Yui and Sandforf. [29].	Two heavy gasoils with similar TBP curve (232°C-551 °C) and (291°C-522°C)	VGO hydrocracking over presulfided NiMo/Al <sub>2</sub> O <sub>3</sub> catalysts in a Pilot-scale trickle-bed reactor at 350°C-400°C, 7-11 MPa and 0.7h <sup>-1</sup> - 1.5 h <sup>-1</sup> LHSV.	4	The activation energy for naphtha production is higher than LGO production. Hence, the naphtha/LGO ratio increases as temperature increases.

Table 2-5. Summary of HC mechanisms

kinetic model	Authors	Feed Characteristics	Process	S.N	Conclusions
	Martínez and Callejas et al. [30].	A Maya residuum with a high concentration of nickel (45.17 ppm) and vanadium (242.12 ppm)	Hydrocracking at 375°C, 400°C and 415°C over a commercial catalyst at 12.5 MPa in a perfectly mixed reactor in continuous operation.	5	First-order reactions for the hydrocracking of Maya residuum and obtaining a good agreement with experimental data.
	Aoyagi et al. [31].	Several gasoils with big differences in its boiling points.	Two stage hydroprocessing in a scale-pilot Packed Bed reactor at 380°C and 13.8 MPa with a LHSV of 0.75 h <sup>-1</sup> .	6	The rate of hydrocracking strongly depends of feed of nitrogen due to the inhibition of hydrocracking of saturates to kerosene and naphthas.
	Botchwey et al. [32].	Bitumen-Derived Gas Oil from Athabasca with a boiling range (340°C-550°C) and 0.99g/cm <sup>3</sup> of density	Micro trickle-bed reactor with a commercial NiMo/Al <sub>2</sub> O <sub>3</sub> catalyst at constant temperature, 360°C, 380°C and 400°C.	7	The yield of lighter products such as gasoline, kerosene and light gas oils were highest at highest temperatures (420°C)
	Sánchez et al. [33].	Maya Heavy crude with same properties of Martínez experiments.	hydrocracking of Maya residuum with a Ni/Mo catalyst at 380°C-420°C and 0.33 h <sup>-1</sup> -1.55 h <sup>-1</sup> of LHSV in a fixed-bed down flow reactor.	8	The mechanism was capable to predict the production of unconverted residue into VGO, distillates, naphtha, and gases with an average absolute error of less than 5%

## 2.2. Fluid catalytic cracking

### 2.2.1. Process description

Catalytic cracking process is one of the main on refinery. Several high-value commercial products such as gasoline and diesel are produced in this unit by cracking or decomposition of gas oil on a catalytic surface. The process uses VGO as raw material. The VGO coming from DC constitutes the main raw material for FCC.

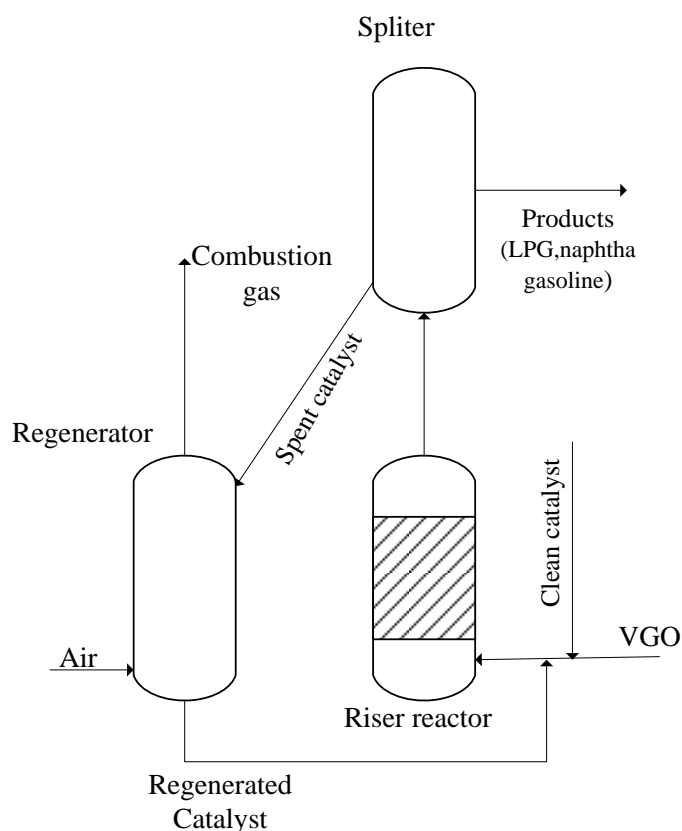
Figure **2-3** describes a FCC process. Feed entering to the riser reactor consist mainly of VGO mixed with regenerated catalyst from the regenerator. In most of the cases, FCC unit uses spherical catalyst that behaves like a liquid when it is fluidized with the entering VGO.

A stream that contains only fresh catalyst is also a part of the entering streams. During the reaction, separation and regeneration, catalyst particles may break and subsequently lost in emissions. To compensate this loss, another entering stream of clean catalyst is required. Also, this stream provides a fraction of the required energy for the FCC process. Figure **2-3** also describes the entering air that burn the coke in the regenerator through combustion reactions. The exit stream from the regenerator consists mainly by  $\text{CO}_2$ ,  $\text{H}_2$ , and vapor. The splitter separates the light products from catalyst, the latest goes to the regenerator whilst, light products are subsequently separated into LPG, naphthas and gasoline.

Most of the FCC units have mainly two equipments. An ascendent flow reactor (Riser) or descendent flow reactor (Downer), where the interaction between feedstocks and catalyst takes place, and a regenerator. Regenerator burns the coke, previously formed in the reactor due to thermal cracking reactions, to clean or regenerate the catalyst. Despite of there are other equipments in the FCC unit, this thesis will focus mainly in the above mentioned.

#### 2.2.1.1. Riser reactor

At present, most of the reactors from a FCC unit are riser reactors. In this case, the interaction between the feedstock and catalyst is slow, around three to ten seconds. The cracking reactions take place instantaneously in vapor phase on a catalytic surface after the feed is vaporized. After thermal cracking reactions take place, the reactor temperature decrease due to the endothermic nature of this reactions. Raw material is fed to reactor with hot catalyst



**Figure 2-3.** FCC conceptual scheme

(around 800 K) coming from the regenerator, which provides the necessary energy to thermal cracking reactions take place. Finally, the light products Gasoline, Liquified Petroleum gas (LPG) are separated from the catalyst, and the last one goes to the regenerator.

### 2.2.1.2. Regenerator

In the regeneration process, air enters the regenerator completely mixed for a subsequent coke combustion. The clean and regenerated catalyst recirculates to the reactor either in counter current flow or concurrent flow depending of the type of reactor. During the coke combustion, the catalyst temperature increases given that the reactions are highly exothermic, hence, the catalyst recirculation from regenerator provides the necessary energy to the reactor in order to favor the cracking reactions.

FCC regenerators usually consists of a large fluidized bed reactor and has mainly two zones: the dense region and the dilute region. The reactions occur in the dense region, where the concentrations of gas and solid are high. In the dilute region the catalyst particles are carried away to return them back to the dense region.

The gas flow is divided into bubble and emulsion phases in the dense region. Most of the combustion reactions occur in the bubble phase, which has the necessary gas to fluidize the solids. The emulsion phase consists mainly of excess of gas, hence, the modeling of regenerator could be approximated as a Current Stirred Tank Reactor (CSTR) or Plugged-Flow Reactor (PFR).

The catalyst regeneration could occur in two ways depending on the type of combustion in this process: partial combustion or complete combustion. Depending on the interest during the process, the complete combustion can be preferred for increasing the energy production and decreasing the coke yield. Otherwise, the partial combustion can be preferred for generating less energy and increase the coke yield. On this way, the excess component for each type of combustion are the oxygen and carbon respectively. This implies, for the partial combustion case, an increasing on the coke yield which leads to coke formation instead  $\text{CO}_2$ .

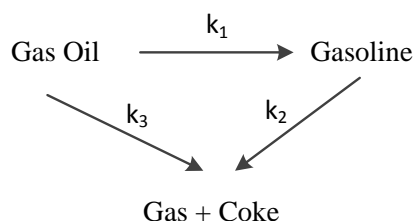
## 2.2.2. kinetic mechanisms

### 2.2.2.1. Reactor mechanisms

Similarly to HC mechanisms, the kinetic mechanism for FCC uses a lumping methodology to represent the process. Weekman et al. [4] proposed a three-lump mechanism presented in Figure 2-4, which includes two second-order reactions for the decomposition of VGO into gasoline, gas and coke. The authors considered also a first-order reaction for the decomposition of gasoline into gases. This lump-mechanism was the pioneer for the catalytic cracking process. This kinetic model was further extended to several other kinetic schemes as the model proposed by Lee et al. [36] and Theologos and Markatos [37, 38]. The mechanism predicts the conversion of raw material into gasoline. However, despite of to consider the coke formation, it does not consider the coke as an independent lump, but it groups coke into a lump which also contains the remaining compounds except gasoline ( $\text{C}_5$ -210°C).

Coke formation must be predicted wit a high level of accuracy, thus, It was necessary to





**Figure 2-4.** Three-lump kinetic mechanism proposed by Weekman et al. 1969 [4]

predict this phenomenon and include it as independent lump as product of cracking reactions. Therefore, more detailed mechanisms were developed. A ten-lump mechanism proposed by Jacob et al. [1]. Lumping using pseudo-components was based in the boiling point of each one also in the chemical structure for hydrocarbons in the mixture. The compounds was grouped in paraffin, naphtenes, aromatics, high and low boiling point, gasoline and coke as show table 2-7.

Table 2-7 describes with more detail the VGO decomposition into gasoline. In this mechanism gas oil was represented by high boiling point compounds (Ph, Nh, Ah, Ch). these lumps react to form low boiling point compounds (Pl, Nl, Al, Cl) and after react to produce gasoline and coke. Also, the mechanism describes all the possibles pathways to coke formation, all of them by second order reactions except the pathway from gasoline lump. This mechanism was also object of study from many researches that included mechanism reduction such as those developed by Coxon and Bischoff [39]

Jacob's mechanism has a more accurate prediction than Weekman's mechanism. Jacob's mechanism also consider the catalyst deactivation due to the coke formation as later Theologos et al. [38] proved. Another factor is the the characterization of raw material, this can be determines how the initial composition of heavy oil affects the production of light compounds and coke and the mechanism may be used to model any kind of residue oil.

**Table 2-7.** Ten-lump mechanism proposed by Jacob et al. [1]

from	to	AE (Btu/lb-mol)	rate (1/S)*	HOR (Btu/lb)
Ph	Pl	26100	0.196	25
Nh	Nl	26100	0.196	25
Ah	Al	26100	0.196	25
Ah	Rl	26100	0.489	25
Rh	Rl	26100	0.049	25
Ph	G	9900	0.611	65
Nh	G	9900	0.939	65
Ah	G	26100	0.685	65
Ph	C	31500	0.099	225
Nh	C	31500	0.149	225
Ah	C	31500	0.198	225
Rh	C	31500	0.149	225
Pl	G	9900	0.282	40
Nl	G	9900	0.752	40
Al	G	26100	0.196	40
Pl	C	31500	0.099	200
Nl	C	31500	0.099	200
Al	C	31500	0.050	200
Rl	C	31500	0.010	200
G	C	18000	0.048	160

Given its detail, Jacob's mechanism, has been used in the study and modeling of riser reactors [38], some authors developed subsequent changes to the mechanism in order to get a better predictions of experimental data. One of them, was done by Barbosa et al. [2], which included a new lump called Dry Gas, as shown in table 2-8.

**Table 2-8.** Eleven-lump mechanism proposed by Barbosa et al. [2]

from	to	rate (1/S) x 10 <sup>2</sup> *	AE (J/kmol)
Ph	Pl	60	0.196
Nh	Nl	60	0.196
Ah	Al	60	0.0049
CAh	CAI	60	0.196
Ph	G	23	0.611
Nh	G	23	0.939
CAh	G	60	0.685
Ph	C	73	0.099
Nh	C	73	0.149
Ah	C	73	0.149
CAh	C	73	0.198
CAh	Al	60	0.489
Pl	G	60	0.282
Nl	G	60	0.752
CAI	G	60	0.196
Pl	C	73	0.099
Nl	C	73	0.099
CAI	C	73	0.050
Al	C	73	0.010
G	C	41	0.048
HFO	DG	60	0.196
LFO	DG	60	0.282
G	DG	42	0.048
C	DG	42	0.048

During catalytic cracking, thermal cracking reactions could occur due to an increase in the operational temperature. Because of this, the authors proposed this lump (Dry gas) to represent the gaseous products formed from thermal cracking reactions. The mechanism was used to CFD simulations. The results showed a good fitting according to experimental data for different residue oil.

Despite it is expected that the recent mechanism have a higher detail level that includes more lumps or pseudo components, several authors preferred to propose changes for the

mechanism proposed by Weekman et al. [4]. On this way, Lee et al. [36] proposed a four-lump mechanism, it was the first modification to Weekman's mechanism. The main changes consist in the separation of coke as an individual lump, therefore, the velocity of coke deposition could be calculated from gas oil decomposition. Consistent with the mechanism proposed by Weekman, the VGO decomposition is represented by second order reactions, whilst, gas and coke formations from gasoline are represented with first-order reactions.

Because of the smaller number of lumps, Weekman's mechanism has been widely used for modeling and CFD simulations in riser reactors. One example is the study developed by Corella et al. [40] that included a mathematical model with the catalyst deactivation due to coke formation. More recent studies have used the Weekman's mechanism for developing a CFD approach, One of this, developed by Ahsan [41]. Results showed a good fitting with temperature and concentration profiles along the riser reactor. Further CFD simulations were developed by Ahsan [42] using the kinetic proposed by Gianetto et al. [25] obtaining results with a good fitting with experimental data obtained from Riser simulator. Finally, a comparison between these two mechanisms using CFD simulation was developed by Ahsan [26] in order to determine the accuracy of each kinetic model to represent one set of experimental data reported in literature [18, 43], which concluded both mechanisms presented good agreement according to experimental data.

The mechanism proposed by Lee et al. [36], as a modification from Weekman's mechanism was widely studied, mainly because the mechanism consider the gas lump, but the information about its characterization was limited. On this way, Some studies focuses in to develop a mechanism with a higher detail for the Gasoil, Gas and Gasoline lumps [44–47]. Ancheyta et al [45, 46] proposed separation of the last lump (gas) into LPG and Dry Gas, the first one are  $C_1$  to  $C_3$  gases, while the other included  $C_4$  gases. While Hagelberg et al. [47] proposed the characterization of the Gasoline lump using PANO methodology, which represents the lumps using paraffin, aromatics, naphthenes and olefines.

The future in the modeling of CFD simulation goes to the development of more detailed mechanisms, as those proposed by Pitault et al. [48] that includes 19 lumps and 25 reactions. In this work, the authors proposed one deactivation factor by coking for all of reactions, except for reactions that lead to coke formation. The mechanism proposed here had further applications in hydrodynamics modeling such as those developed by Derouin et al. [49]. Recently, a kinetic model based on a semi-empirical approach using a normal probability function was developed by Gupta et al. [50]. The high-level of detail allows to work with

a large number of lumps because kinetic parameters were determined by feed conditions, catalyst activity and coke formation tendency on the feed.

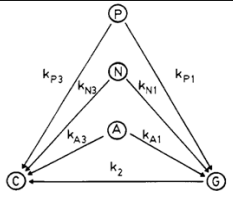
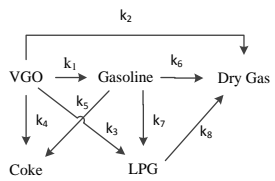
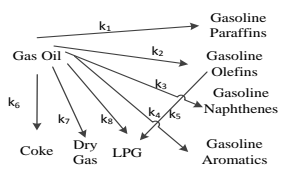
#### **2.2.2.2. FCC mechanisms Summary**

Next tables (2-9) and (2-11), show a summary of the FCC mechanisms. This revision consists mainly in the most important features for each mechanism to represent the fluid catalytic cracking. For each mechanism, the table shows the kinetic model, the feed features, operational conditions of the experiments, and the main conclusions and contributions.

Table 2-9. Summary of FCC mechanisms

Kinetic model	Authors	Feed Characteristics	Process	S.N	Conclusions
	Weekman et al [4].	Gas oil with API gravity equal to 29.6° and boiling point range between 423 y 904°F (490-758K)	Fixed and fluidized bed reactor at constant temperature. Commercial TCC zeolite.	1	Catalyst deactivation function decrease while gasoline and gas oil is cracked. Activation energy values are different for gasoil and gasoline cracking.
	Jacob et al. [1]	Gas oil with boiling point between 650 y 959°F (343-788K). Characterization by mass spectroscopy to calculate naphthenes, paraffin and aromatics compositions.	Fluidized bed reactor with residence time between one to five minutes at 900°F (755K).	2	Kinetic constants computation are independent from gasoil composition. It was included the effect of operational conditions of the reactor in the kinetic parameters.
	Barbosa et al. [2].	The same feed conditions used by Jacob et al. [1]	CFD simulation for a riser reactor of 34.2m of height and 0.8 m of diameter. Gasoil flow between 20 y 48 kg.m <sup>2</sup> .s <sup>-1</sup> at temperature between 500 y 600K.	3	Good prediction of gasoline yields with respect experimental data. It was demonstrated there are thermal cracking reactions, and its effects could be reduced if there are a good mix between gas and catalyst.
	Lee et al [36]	Same feed conditions used by Weekman et al. [4]. because this mechanism is a modification from Weekman.	High active catalyst. Isotherm reactor at 550K approximately.	4	The values corresponding for the gas oil conversion and gasoline cracking are fitted according to the experiments. The model predicts the coke formation because it is considered as a independent lump.

Table 2-11. Summary of FCC mechanisms

kinetic model	Authors	Feed Characteristics	Process	S.N	Conclusions
	Larocca et al. [44].	Two gas oils with boiling point between 534K and 482K to 817K. Their compositions and molecular weights are so different	PFR reactor at constant pressure and temperature. Second order constants to gas oil cracking.	5	Raw material represented by paraffin, naphthenes and aromatics. The catalyst deactivation function shows a good agreement with kinetic constants under short contact times between gas oil and catalyst.
	Ancheyta et al. [45].	Gasoil from Tula refinery with boiling point between 508 and 841K nad $Al_2O_3$ catalyst.	The experiments were carried out in an isothermal batch reactor at 480, 500 y 520°C and a catalyst-oil ratio equal to 5.	6	A new lump was considered LPG, that represent gases ( $C_1-C_3$ ). The detail level is so important to predict important species that are produced in FCC such as propane.
	Hagelberg et al. [47].	Hydrotreated gasoil with low contents fo metals and sulfur and boiling point between 141°C and 405°C and a commercial catalyst wit particle size of 80 micrometers.	The experiments were carried out in a isothermal PFR at 400°C and 650°C and catalyst-oil ratio between 2.6 and 2.95. and low residence times (0.03-0.09s).	7	The model predicts the yields of PANO reactions from gasoline. The catalyst activity weakly depends with coke formation in the catalyst under short contact times.

### 2.2.2.3. Regenerator mechanisms

Unlike to kinetic mechanism for HC and FCC, the mechanism that represent combustion reactions in the regenerator does not use the lump methodology with pseudo components. Most of these mechanisms use global pathways for known compounds such as carbon, oxygen, hydrogen, etc. The kinetic mechanisms for the regenerator assume that coke is composed by carbon and hydrogen despite having an amorphous and variable structure. In the practice, coke is composed in less proportion by sulfur and nitrogenated compounds. However, despite the differences that exists in the coke composition, there are not a significant difference when the combustion in the regenerator is modeled [51].

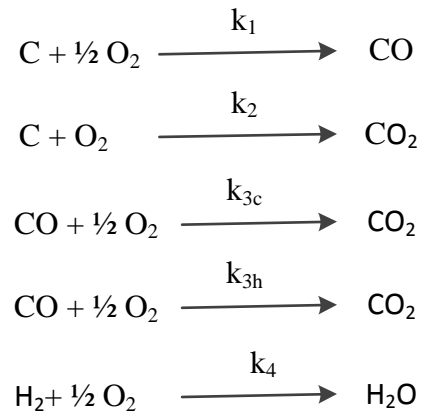
Arbel et al. [5] proposed a mechanism for carbon combustion that consists in four reactions for the catalyst regeneration as presented in Figure 2-5, which shows the main reactions that occur in the regeneration process. Most of them are combustion of carbon and global reactions in order to simplify the reactions of combustion in the regenerator. Figure 2-5 shows the reaction for  $\text{CO}_2$  represented with the  $k_{3c}$  that is not taking into account due to this is complete and immediate. Despite of the fluidize zone of regenerator can be modeled as a PFR reactor, the authors model the regenerator describing the plug flow as a CSTR cascade by assuming a quasi-steady state approach.

More recent kinetic mechanisms for the regenerators has also considered that the reactions carried out in this equipment are carbon oxidation reactions, CO combustion and, in some cases, hydrogen combustion [52,53]. However the type of reactor that is used to model the regenerator, temperature conditions and the experimental data, leads to significant differences in the kinetic parameter values.

The FCC technology has more than 60 years, however, the study of coke combustion reactions in the regenerator being developed in the 80's. The mechanisms were based on empirical or semi-empirical approaches that leads to errors in the modeling and hence in the fitting with experimental data. Moreover the proposed mechanism by Effects et al. [54] leads to successful results with his own approximations for each case. They assumed that gas flow was greater in the dense zone of the reactor and it could be modeled as PFR, hence, its leads to predict relevant factors during the process such as  $\text{CO}_2/\text{CO}$  ratio in regenerator obtaining the same results of Weisz and Goodwin [55].

The mechanism proposed by Fernandes et al. [52,53] considered two zones in the regenerator and had a good prediction and fitting with experimental data. They assuming an instanta-





**Figure 2-5.** Five-reactions kinetic mechanism proposed by Arbel et al. 1995 [5]

neous equilibrium between catalyst flow and air in the down zone of the regenerator. In the upper section, the reactor was modeled as an pseudo steady-state PFR in which combustion reactions occur. Also, taking into account the equilibrium assumption in the down zone, gas and catalyst combustion was simulated as PFR reactor. Also, the authors describes the same reactions that Arbel et al. [5] as shown in Figure 2-5 .

Previously, Arandes et al. [6,7] had proposed a two-reactions mechanisms for the coke regeneration. Figure 2-6 shows the mechanism that also consider the H<sub>2</sub>O formation due to the combustion reactions. But it considers a CO/CO<sub>2</sub> molar ratio called by them for the Greek letter beta that represents the type of combustion in the regenerator.

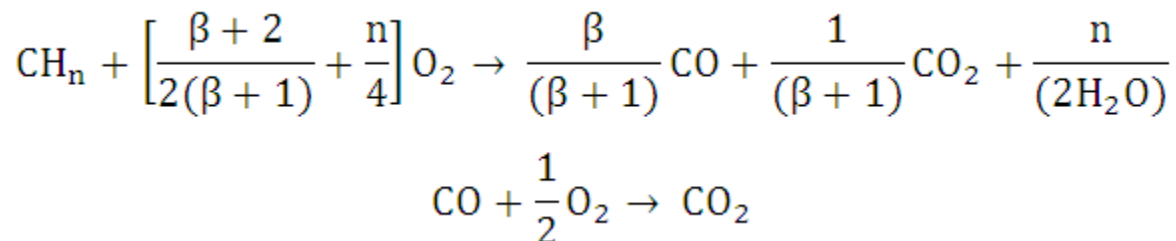


Figure 2-6. Two-reactions kinetic mechanism proposed by Arandes et al. 1999 [6, 7]

## 2.3. Delayed coking

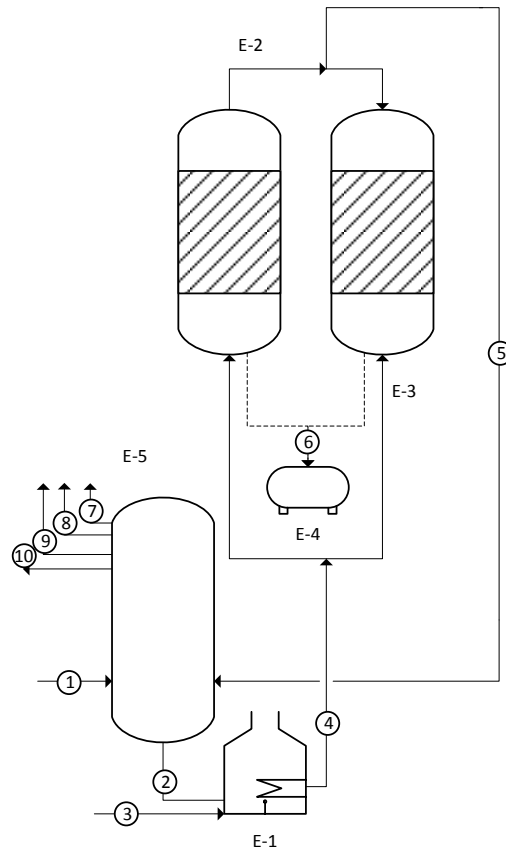
### 2.3.1. Process description

The DC drum is the main equipment from the DC unit. Its function is to convert the heavy residues (VRC) from vacuum towers to coke and recovery valuable compounds such as naphtha, gases, and in some cases gas oil for a subsequent treatment in FCC units. A further main fractionator separates all the gases that came from the DC unit. In refineries, the DC process works as a semi-continuous process using two coke drums in a parallel array. Given that the coke is deposited in the drum, after filling, the entering VRC is suspended and it is connected to the parallel drum to make the cleaning of the first drum. To recover most valuable compounds, it is necessary to heat the feed until the cracking temperature (around 773 K or 932 °F) in a previous furnace before the drum. VRC goes through out the furnace with a short residence time (1-3 minutes) and subsequently goes to the drums previously described.

Figure 2-7 shows a scheme for delayed coking. VRC heats the stream 4 which goes to coke drum. VRC reacts by effect of temperature to produce, in this case, light and heavy coker gas oil, naphtha, and gases, all of them in the stream 5. After thermal cracking, stream 5 goes to a main fractionator which separates each compound according to their boiling points (stream 7, 8, 9, 10). Unconverted VRC (stream 2) goes to the tubular furnace which heat it in presence of hydrogen or water (stream 3) to avoid the coke formation in its walls.

One of the main functions of DC unit in addition of light products formation, is to maximize

the coke formation into the drums in order to avoid as much as possible the coke formation during the crude oil processing in the other refinery processes. The more valuable products in this process are naphtha and gas oil, that works as raw material for subsequent refinement process as FCC and HC.



**Figure 2-7.** Schematic figure for Delayed Coking process

### 2.3.2. Kinetic mechanisms

The low availability of kinetic mechanisms to represent the delayed coking process is mainly due to the complexity of reactions that take place here. The variability on composition of heavy oil from vacuum distillation tower implies that mechanisms may not represent the thermal decomposition reactions in DC process.

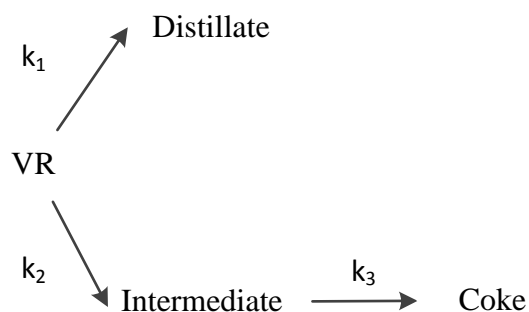
Literature reports kinetic mechanisms for processes that transform residues from vacuum tower into liquid distillables [8–11, 27]. The processes are visbreaking, thermal cracking in tubular furnaces, eureka process, and DC. In these processes, the coke formation is due to pyrolysis reactions. These reactions limit the conversion of raw material into distillable products. Although the reactions are the same in each process, the operating temperature, residence times, and interesting products are different.

Kinetic approaches in literature for DC include the use thermal cracking mechanisms for VRC or heavy residues, it is because the low availability of kinetic mechanism for DC due to also the low availability of experimental measurements made in coke drum. The last approaches assumed that pyrolysis reactions in liquid phase also take place in the delayed coking. Another assumptions, such as assuming that the gaseous phase is irrelevant could be made because it does not affect the product composition. [56].

A mechanism using SARA methodology that represents the VRC as saturates, aromatics, resins and asphaltenes to model DC process was proposed by Zhou et al. [27]. It is a eleven-lumps mechanism that predicts the naphtha yields at the exit of the reactor, and its variation according the SARA composition of entering crude oil. Unfortunately, these authors do not present kinetic data, hence, this mechanism will not be studied in this thesis.

Mechanisms have been reported to represent delayed coking as the mechanism proposed by Del Bianco et al. [8]. This mechanism included a general decomposition of VRC without feedstocks characterization. The authors carried out experiments in a batch reactor under temperature conditions between 410°C to 470°C with a residence time of two hours in order to evaluate the coking of Belaym VRC and to evaluate the formation of distillable products during the thermal cracking.

Figure 2-8 shows the three-lump mechanism proposed by Del bianco et al. [8]. The mechanism included VRC, coke and distillates product as an independent lump, and considered first-order reactions. This mechanism was one of the first which take into account the induction period of coke formation and its variation with temperature. The mechanism also included an intermediate lump that leads to coke formation but this was included only to fit the mechanism to experimental data because was impossible to determine the intermediate concentration through the experimental measurements.



**Figure 2-8.** Four-lumps kinetic mechanism proposed by Del Bianco et al. 1993 [8] VR: Vacuum Residue Crude Oil;

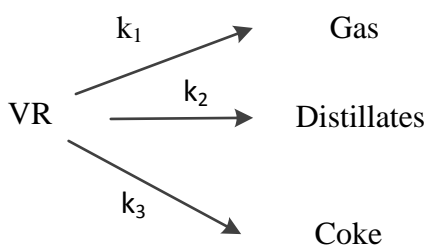
Despite the unavailable data for the kinetic mechanism proposed by Zhou et al. [27], and considering that Del Bianco's mechanism has low detail, a literature review about thermal cracking mechanism was done. The revision involves kinetic mechanisms for thermal cracking in tubes, visbreaking and eureka processes. Although the processes have some differences, the use of those mechanisms could be a first approximation to represent the delayed coking process.

The thermal cracking mechanisms predicts the heavy oil crude oil decomposition considering as a important factor the coke formation. [8–11, 27, 56, 57]. The mechanism proposed by Koseoglu et al. [57] was the first to consider that coke formation strongly depend of asphaltene decomposition. Hence, they considered asphaltene as the main coke precursors during thermal cracking of heavy crude oil.

However, experiments showed this process has a period in which the coke formation is nule. This period is called induction period [58, 59]. Also it was considered that induction period was due to separation phase during thermal cracking. Another authors considered that the coke formation occurs due to the insoluble decomposition and it was determined that this phase corresponds to asphaltenes precipitation [11].

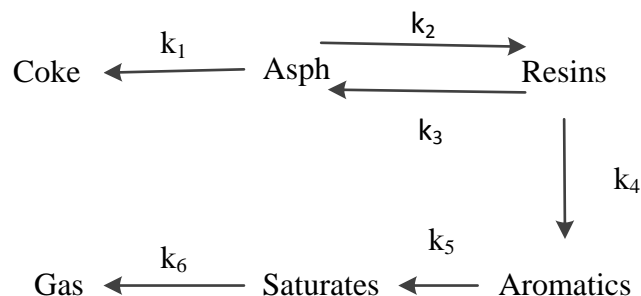
Sawarkar et al. [9] developed a similar procedure, using an Arabian VRC with different pro-

perties. The experiments were carried out in a batch reactor with a temperature between 430°C and 475°C. Sawarkar proposed a four-lumps mechanism as shown in Figure 2-9 and three first order reactions to represent the coking of Arabian VRC.



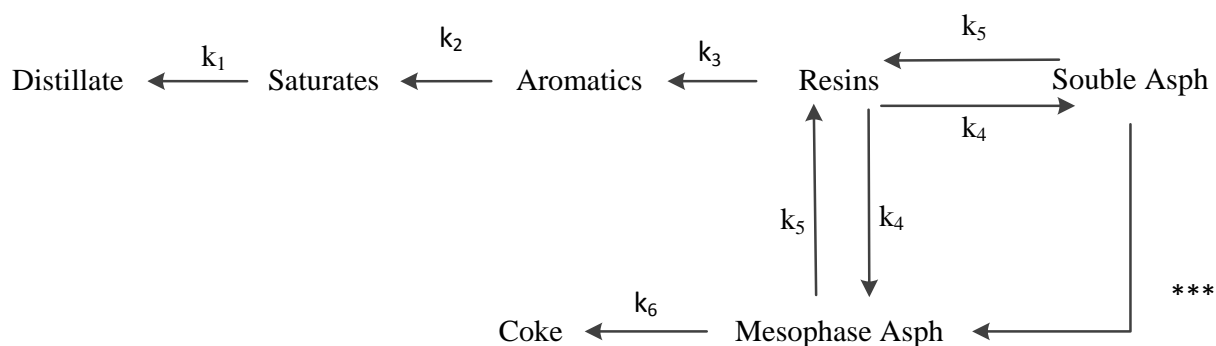
**Figure 2-9.** Four-lumps kinetic mechanism proposed by Sawarkar et al. [9] VR: Vacuum Residue crude oil

Neither the mechanism or products characterization were developed through the SARA methodology, another mechanisms such as proposed by Koseoglu et al. [10] and Filho [11] used this methodology to grouped the heavy oil fractions. Koseoglu et al. [10] proposed the six-lumps mechanism as shown in Figure 2-10. The experiments were carried out in a batch reactor between 385°C and 420°C using Athabasca bitumen as feedstock. The mechanism was developed to determine and evaluate the yields of each lump during thermal cracking. This mechanism was succesfully adapted for thermal cracking process in a tubular furnace [60].



**Figure 2-10.** Six-lumps kinetic mechanism using SARA methodology , proposed by Koseoglu et al. [10]

Subsequently, Filho [11] proposed a change for the last mechanism. This change considered an intermediate lump that leads to coke formation as shown Figure 2-11. Filho concluded that the intermediate was mesophase or precipitated asphaltene. This asphaltene was produced due to its solubility decreased when the resins reacts, that works as a soluble agent for asphaltenes. The precipitation is irreversible and leads to coke formation due to temperature effects.



**Figure 2-11.** Seven-lumps kinetic mechanism using SARA methodology , proposed by Filho et al. [11]

Another mechanism which represents the coking and VRC decompositions was studied, in this case to represent reactions that occur in the eureka process [61–70]. Although the operational conditions were different, it was possible to determine pathways for VRC decomposition into light products and coke during delayed coking process.



## 3. Methodology

This Chapter presents the methodology employed for the development of this thesis. First, a description about how experimental data taken from literature were grouped using XML. Chapter also shows the main advantages of XML, its implementation and previous applications and its importance in the future of chemical processes modeling and simulation. Chapter presents as well the equations that govern the thermal decomposition processes previously explained in this thesis. Finally, Chapter describes all the methodology carried out to get the kinetic parameters and their respective uncertainties. The methodology includes: a) Lumps selection for the mechanism; b) kinetic parameter estimation through optimization routines available in Matlab 2014 and finally, c) uncertainty calculation through statistic techniques. Although there are some similarities in the methodology for each process, some steps presents considered important changes that will be described in detail later.

### 3.1. Catalytic Hydrocracking

#### 3.1.1. XML (eXtensible Mark-Up Language) data standardization

The procedure begins with the building of a database that enable to unify and standardize all the information taking from literature. Generally, these studies in the available literature about petroleum refining proposes an individual set of kinetic parameters. The data obtained by other groups is normally lost, or in the best case, only used for comparisons. Hence, this is one of the main problems which this thesis want to face.

This thesis uses eXtensible Markup Language (XML) as the fundamental code to stock the data available in literature for the developing of kinetic mechanisms. Several authors have included in their optimization models and uncertainty calculations with database in XML format [71, 72]. XML is an open source code, it implies that any database can be used for

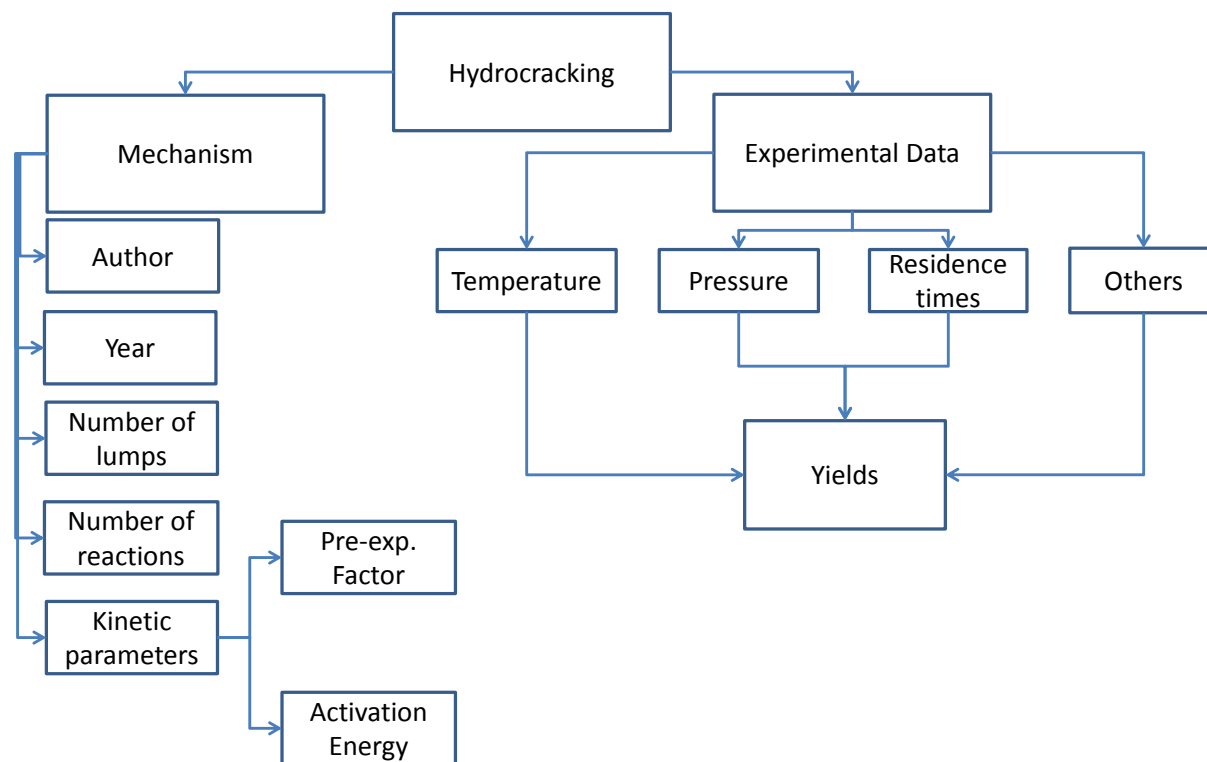
many users around the world. Also, another advantage using XML is the easy reading for any modeling or optimization software. XML schema has been successfully used for the IC engine data model reported by Smallbone et al. [73] and Brownbridge et al. [74], who also use an advance software tool, MoDS (Model Development Suite) for their model validation and visualization.

XML was also considered because it has a tree-like structure that enables a easy readable using any programming language and a better visualization about the featuring that were taken into account for the database building. This thesis proposes a tree-like structure to stock the experimental data for HC. Figure **3-1** shows the tree-like structure and show how the information about HC is organized. The data base has a father node called *Hydrocracking* which has two nodes, those are, *Kinetic mechanism* which includes all the information regarding with the year which it was proposed, number of lumps and reactions and the kinetic parameter information. The other node, *Experimental data* which has all the information about the process conditions of each experiment. The node also has an important variable, the *yields* which represent the yields of each lump and the process conditions under this yields were obtained.

It was possible to storage a wide set of experimental data. For hydrocracking case, a wide range of temperature between 360 and 450°C was obtained with the data recompilation, as well as a range of Liquid Hourly Space Velocity (LHSV) between 0.8 and 1.5 h<sup>-1</sup>. The range obtained for the most important process conditions for hydrocracking enable us to get a mechanism that not only represents with a good accuracy the experimental data from literature but is also, unless the previous researches, can works in one wide range of process conditions, thus becoming in a general mechanism.

### 3.1.2. Lumps selection

The XML database suggests a starting point to select the the number of lumps and reactions that the final mechanism should have. From the information in the XML the lump mechanism selected for the final regression process was the one that represented a compromise between the number of lumps modeled and the complexity of the system. Mechanisms with a large number of lumps were not considered as there is not experimental data to fit the parameters. Conversely, mechanism with very few lumps were discarded as they do not give enough detail to represent the process.



**Figure 3-1.** Tree-like structure used in this thesis for data storage taken from literature for HC.

The mechanisms proposed by Martinez et al. [12] describes a decomposition of an atmospheric residue into VGO and light products during a one-step hydrocracking. Since the configuration showed in Chapter 2 about the two-step hydrocracking considers VGO (Figure 2-1)) as a feedstock, we propose a mechanism that only includes the pathways of VGO decomposition and lighter products formation from VGO. Therefore, the mechanism proposed here has 12 kinetic parameters.

### 3.1.3. Modeling and equations

Firstly, the kind of reactor model used to simulate the hydrocracking process will be discussed. A subsequently validation of the mechanism with the experimental data taken from literature previously stored in the XML database includes the simulation of the model used in each source. Despite of the HC process is a non-isothermal process, most of authors ca-

ried out their experiments in batch reactors at constant temperatures in a adequate range for HC, thus, it was possible to find the values for activation energies and pre-exponential terms. Therefore, this thesis will use the batch reactor model to represent the kinetic studies collected in the XML database.

Assuming that the reactions rate follows the Arrhenius law and the model only considers temperature and liquid residence time, and given that the model does not include the total system pressure as it neglects any mass transfer restrictions and the reaction rates only involve the mass fraction of each lump. The HC could be represented as a set of first-order and irreversible reactions as shown in the (Eq. 3-1). These approximations would be valid in the case were the hydrogen concentration in the liquid phase would be high enough so that the kinetic reaction of hydrogen with the VGO and derivatives would be the limiting step. Also, if it is taken into account that lump-mechanisms could be represented as an implicit kinetic where each kinetic parameter includes the hydrogen concentration as well as the mass transfer phenomena and the catalyst properties, these last features could not affect the final product yield.

The reactions for HC process are those that represent the Vacuum Gas Oil decomposition to produce light compounds like diesel, naphthas and light gases. The equations are shown below (Eq. 3-1) where  $y_i$  represent each lump in the HC mechanism

$$\frac{dy_i}{d(LHSV^{-1})} = \gamma_i \quad (\text{Eq. 3-1})$$

Because of all reactions are first order reactions, the equations to calculate the velocity constants are the same and follow the Arrhenius expression. These equations are shown below (Eq. 3-2).

$$k = A \times \text{Exp} \left( \frac{-E_a}{RT} \right) \quad (\text{Eq. 3-2})$$

For HC, the system that represent all the mass-conservation equations is given by the next set of equations:

$$\begin{aligned}\frac{dy_{VGO}}{d(LHSV^{-1})} &= -(k_1 + k_2 + k_3)y_{VGO} \\ \frac{dy_{Distillate}}{d(LHSV^{-1})} &= k_1y_{VGO} - (k_4 + k_5)y_{Distillate} \\ \frac{dy_{Naphtha}}{d(LHSV^{-1})} &= k_2y_{VGO} + k_4y_{Distillate} - k_6y_{Naphtha} \\ \frac{dy_{Gas}}{d(LHSV^{-1})} &= k_3y_{VGO} + k_5y_{Distillate} + k_6y_{Naphtha}\end{aligned}$$

### 3.1.4. Kinetic Parameter Estimation

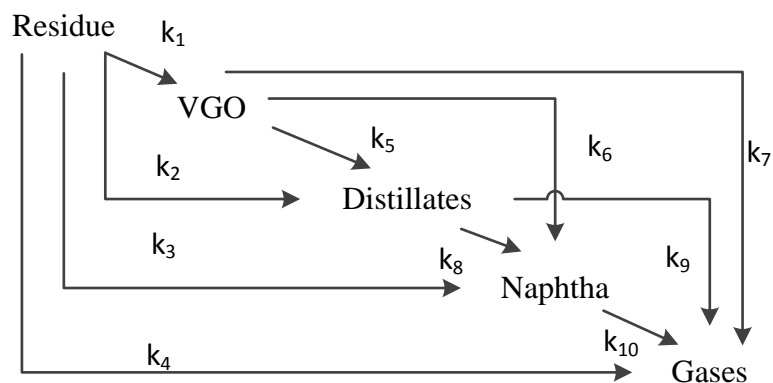
A total of 99 experimental data corresponding to five different sources were taken into account to make a general fitting and get the best set of kinetic parameters for hydrocracking process. The figure **3-2** shows the original mechanism proposed by Martinez and Ancheyta [12] and the modification employed in this thesis as shown in the figure **3-3**.

We observed during the optimization process, the kinetic parameter values strongly depend on the seed values of each kinetic parameter given in the optimization. The way to calculate the best initial conditions was to generate randomly using a Monte Carlo approach typical values for each kinetic parameter and calculate the value of the objective function as proposed by Assae et al. [35]. We tested 5000 combinations for determining the best initial conditions.

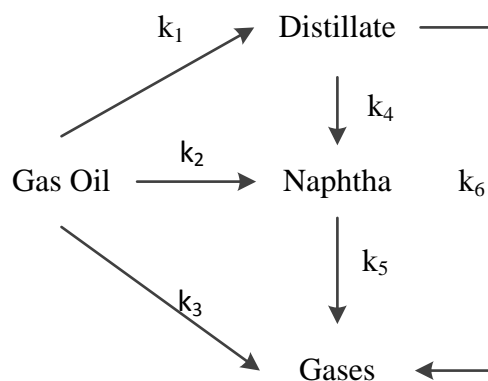
After the database was completed, the *fmincon* routine from Matlab based on the Levenberg-Marquardt algorithm was developed to estimate the corresponding kinetic parameters. The algorithm searches the optimal values that minimize the mean square error (MSE) presented in equation Eq. 3-3, between experimental data and data obtained from this mechanism.

$$MSE = \sum_{i=1}^N (y_i^{pred} - y_i^{exp})^2 \quad (\text{Eq. 3-3})$$

Where N means the number of experimental data from the different sources, in this case, 99, Y represents yield, mass fraction or flows depending on the case, and  $y_i^{pred}$  and  $y_i^{exp}$  are the predicted and experimental yields for each lump in the mechanism respectively.



**Figure 3-2.** Five-lumps hydrocracking mechanism proposed by Martinez and Ancheyta [12]



**Figure 3-3.** Four-lumps hydrocracking mechanism proposed in this thesis.

In statistical terms, the minimization of mean square error is a good optimization which is obtained due to the error of magnitude, this makes it one of the most used function in the optimization routine. However, its application to get the kinetic parameters for hydrocracking

mechanism was not adequate due to the difference in the magnitude order between each lump of the mechanism. It can be observed that values of VGO lump in some cases are close to 1, whilst gas lump considers values close to  $1 \times 10^{-3}$ . The optimization routine using this objective function was evaluated and the results agree with only kinetic parameters associated with bigger lumps were optimized.

To overcome this drawbacks, authors such as Alcazar et al. [75] considered using a weighting factor for each lump, this mean, the methodology optimizes all the kinetic parameters regardless the magnitude order of their values. Alcazar et al. [75] proposes a weighting factor such is shown in Eq. 3-5 where  $w_i$  is the weighting factor equivalent to the inverse root square of each lump value.

Also, (Eq. 3-3), suffered another change. This implies a change in the superscript value. The main reason to change the superscript value was due to the lower values of the objective function during the optimization. This mean that the values corresponding to yields for each lumps are in a range between 0 and 1 are powering to a superscript, in this case, its value is 2, thus, values closer to 0 will be obtained implying a more computational effort for the optimization algorithm and in many cases the solution converged to non logical values. In this case, a value of 0.5, this mean, a root square instead to power to square was used to calculate the final objective function.

Considering the changes mentioned above, a new minimization error function was used. The new Objective function is given by Eq. 3-4 and Eq. 3-5.

$$WSE = \sum_{i=1}^N w_i \left( y_i^{pred} - y_i^{exp} \right)^{0.5} \quad (\text{Eq. 3-4})$$

and:

$$w_i = 1 / (y_i^{exp})^{0.5} \quad (\text{Eq. 3-5})$$

### 3.1.5. Uncertainty Calculation

In Chemical Engineering is so important to determine the uncertainty of the estimated parameters in any case. Techniques such as Montecarlo method, Sobol sequence or any statistical technique include a random generation point. A great number of points are generated in a determined space to calculate the variability of each parameter through the evaluation of its respective objective function.

This thesis proposes a statistical methodology developed and proposed by Efron [76] to estimate the uncertainty associated to each parameter. This methodology is the bootstrap technique which will be explained below.

#### 3.1.5.1. Bootstrap method

The bootstrap method is a simple but powerful kind of Monte Carlo methodology to assess and calculate the distribution of a set of data when the number of data is lower. The bootstrap is useful when the set of data are independent and not enough to determine the how they are distributed. Bootstrap is an old technique, however, the best contribution was given by Efron [76]. His work mainly focused in using Monte Carlo approximation to know the probability distribution of a random sample to estimate some statistical values such as variance of the sample median and the confidence intervals of the sample. The method mainly consist in a re-sampling procedure, keeping the same size than data vector and with repeatability using these data, for estimating the distributions of statistics based on independent observation. The process is repeated a large number of times in order to ensure as much combination as possible from these data. The mean, standard deviation and percentile values taken from the distribution for all of the bootstrap samples give an estimate of the variability of each parameter, hence, the main statistical properties could be calculated including a estimate of the confidence interval for the data. The confidence interval depends of the accuracy previously defined, according with the confidence percentage, it is possible to determine the uncertainties value and confidence interval taking into account the value of the standard deviation of the distribution obtained using bootstrap.

In this thesis, a confidence interval within 95 % was chosen for each kinetic parameter. Therefore, assuming, as first approximation, that the distribution have a normal behavior, the uncertainty values would be two times the value of standard deviation from the distribution.

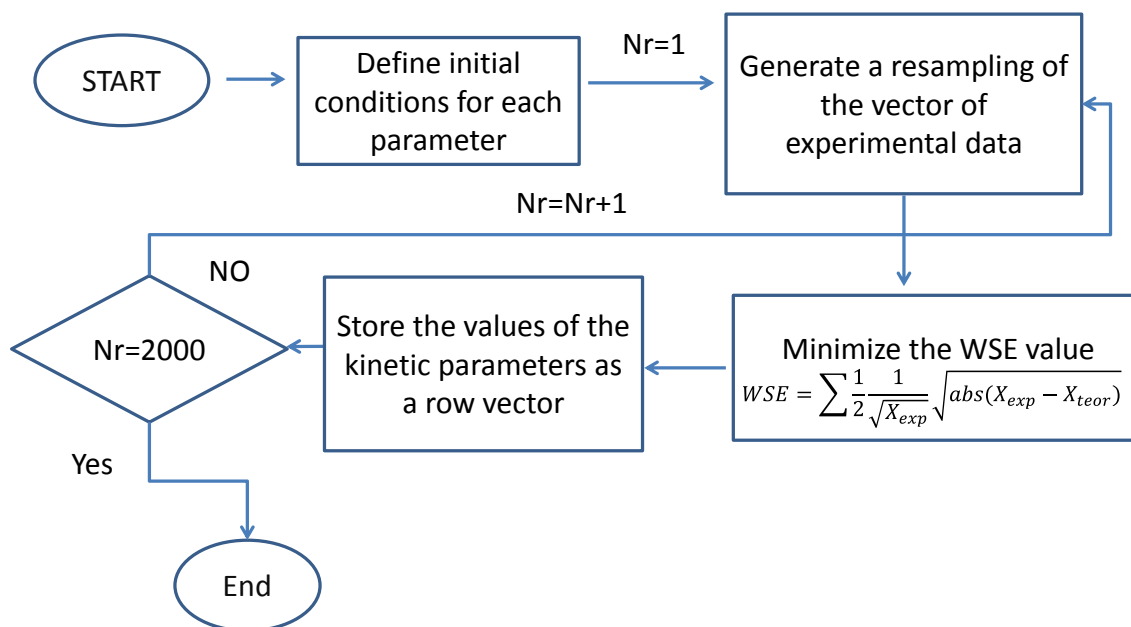


Despite there are many ways to make an uncertainty analysis, such as uncertainty calculation using error propagation methodology or covariance matrix calculation, these techniques were not useful for the uncertainty calculation. The error propagation methodology using an inverse model and applying surface response were developed by Braumann and Kraft [71]. The authors calculate the uncertainty of a kinetic parameters of a model of granulation taking into account the uncertainty associated to experimental measurements. The surface response methodology was used here to decrease the high computational cost associated to solving the large number of differential equation of his system. Although this methodology enable to get a global uncertainty calculation, in this thesis it was not possible because of the lack of uncertainty values related with the experimental data from the refinery literature.

The bootstrap methodology have never been applied before to parameter estimation for refinery process, but it has been widely applied to predict parameters in other cases [77]. The main challenge in this research is to find the way to apply the bootstrapping technique to estimate the uncertainty of the kinetic parameters for the hydrocracking mechanism. Therefore, an algorithm was proposed to calculate the confidence interval for each parameter, although the algorithm does not follow exactly the bootstrap methodology, the bootstrapping methodology was used to make the resampling of the vector of experimental data, and therefore generating a large number of independent samples. The Figure **3-4** summarize the steps that were followed to get the confidence interval for each parameter. The algorithm consists mainly in to make a 2000 resampling of the vector of experimental data. The resampling includes replacement between experimental data, each re sampling has associated a optimization process keeping the same initial conditions for each parameter. Hence, a vector of 2000 samples will be obtained for each parameter. On this way, it is easier to determine the distribution of a large sample, and to calculate the main statistic properties including the uncertainty.

The same steps were followed to get the uncertainty values for Fluid Catalytic Cracking and Delayed Coking. On this way it so important to point out that in the next subsections corresponding to the other process, the uncertainty calculation part will not be present.

The distributions obtained for the parameters corresponding to the same reaction during the uncertainty calculations showed a linear correlation between the pre exponential factor and its respective activation energy. One way to explain this behavior is through the compensation effect theory.



**Figure 3-4.** Algorithm that summarize the bootstrapping technique to calculate the uncertainty of the kinetic parameters.

### 3.1.5.2. The Compensation Effect

The compensation effect has been one of the more controversial areas of chemical engineering [78]. It has been widely reported in literature for many kinetic studies of processes such as: catalytic coal gasification [79]; catalytic steam gasification [80]; coal oxidation at low temperatures [81]. Several literature studies have explained this phenomenon as a mathematical artifact due to the Arrhenius equation [82–85]. Although there is not a direct and physical relationship between the activation energy and the pre-exponential factor, when the compensation effect is evident, a lineal correlation between both kinetic parameters exists, due to an exclusively mathematical artifact.

Given the Arrhenius expression in equation Eq. 3-2, the compensation effect could be defined as the linear relation between the natural logarithm of the pre-exponential factor and the activation energy for a set of kinetic parameters corresponding to the same reaction. Mathematically, equation Eq. 3-2 could be rewritten as the equation Eq. 3-6:

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (\text{Eq. 3-6})$$

Equation Eq. 3-6, shows the linear correlation between the kinetic parameters from the same reaction. Not all of the reactions that follows the Arrhenius equations present such linear behavior. For this case, Figure 4-8 shows a linear behavior given that HC process has first-order and irreversible reactions.

Although many studies have considered the compensation effect as a phenomenon which mostly occur in catalytic systems [86], it also strongly depends of the order of the reactions.

Some advantages of the compensation effect are: to predict the reaction rates and Arrhenius parameters when the data are limited or not enough; to know the effects of the catalyst properties on a surface using explicit catalytic terms; and to provide a tool for determining the governing reaction in the mechanism.

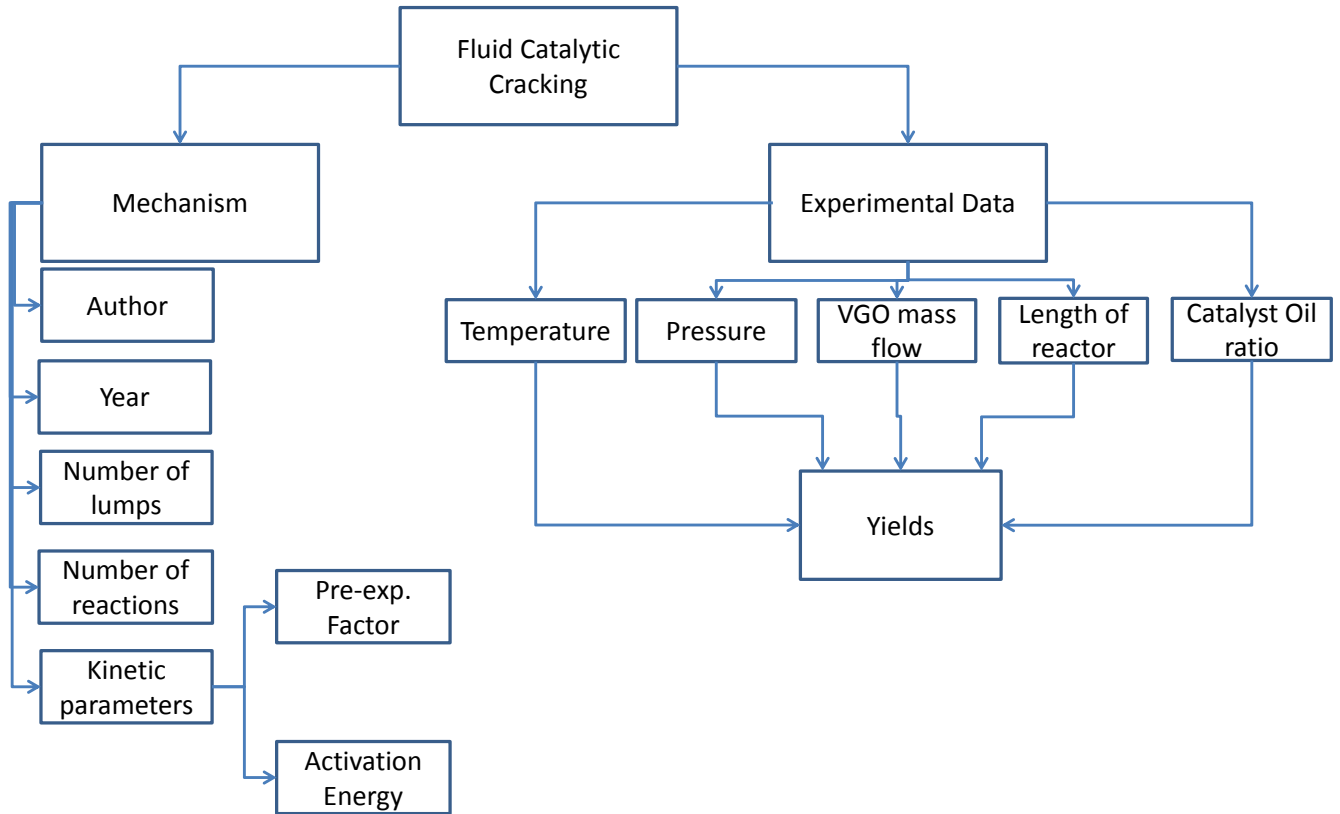
## 3.2. Fluid Catalytic Cracking (FCC)

In this section, a methodology to estimate the kinetic parameter, in this case, for FCC process is carried out. Although the methodology was similar to the last one, it is important to point out some differences that will be explained below.

### 3.2.1. XML (eXtensible Mark-Up Language) data standardization

Unlike HC, FCC database includes more process conditions. However, The database is also built as a tree-like structure to stock the experimental data for FCC. Figure 3-5 shows the tree-like structure and show how the information about FCC is organized. The Tree-like structures consider the same nodes, except those regard to *Experimental data* which has five nodes instead of two as HC. These five nodes represent the most important process conditions for FCC, which were taken into account to make the optimization.

Also for FCC was possible to storage a wide set of experimental data that includes experiments carried out in industrial and pilot case reactors. Table 3-1 shows the range which



**Figure 3-5.** Tree-like structure used in this thesis for data storage taken from literature for HC.

process conditions are changing. Given this wide range for every process condition, and in the case that model shows a good fitting regard all the experimental data, it can be said that the kinetic mechanism becomes into a general mechanism.

**Table 3-1.** Range for each process conditions for the FCC

Properties	Operation Range
Temperature (C)	450 - 550
Pressure (KPa)	200-300
COR	3.5-8.5
Diameter (m)	0.4 - 1.5
Feed rate (kg/s)	2 - 55
Length of reactor (m)	2.5 - 4

A more detailed table below summarizes the process conditions that were taking into account for the development of the mechanism for FCC. The table includes data from experiments that simulated riser reactor, in pilot scale and industrial scale. The main objective here was to evaluate some process conditions and get the mechanism that can give the best approximation for all the data. The most important conditions such as, operation temperature, diameter, length of reactor, density of feedstock, molecular weight of the lumps, yields in the exit of reactor, were taking into account for the database building and to get the mechanism. Table 3-2 show the main features mentioned above for the building of database and the lump-mechanism.

**Table 3-2.** Summary of process conditions stored in the XML database for Fluid Catalytic Cracking

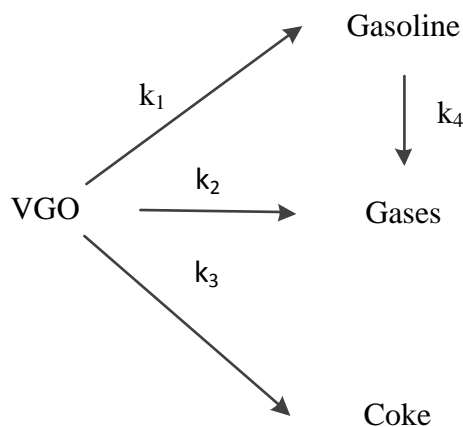
Authors	Ref. [18]	Ref. [19]	Ref. [20]	Ref. [21]	Ref. [21]	Ref. [21]	Ref. [21]	Ref. [22]	Ref. [23]	Ref. [24]
IBP(C)	-	288	-	288	268	253	282	305	305	-
FBP(C)	-	546	-	546	525	526	555	498	498	-
T(C)	522	500	522	494.3	494.4	494.3	494.2	520	520	527
Reactor Length(m)	34.2	36.97	33	37	37	37	37	41.1	41.1	27.5
COR	7.2	6.48	7	4.56	4.99	5.09	4.48	8.1	6	3.7
Diameter(m)	0.8	0.68	0.8	0.7	0.7	0.7	0.7	1.5	1.5	0.4
Feed rate(kg/s)	20	32.14	20	49.3	50.2	46.7	47.2	34.6	34.6	2.6
Pressure (KPa)	200	220	219	230	230	230	230	250	250	220

### 3.2.2. Lumps selection

This thesis considered to take one mechanism from literature for a subsequently estimation of its kinetic parameters. A four-lump mechanism was chosen to represent the FCC. The mechanism originally proposed by Lee et al. [36] as a modification of Weekman's mechanism [4]. The mechanism has 4 lumps: VGO, is the raw material of the FCC; Gasoline represents all the compounds between C8 and C14; Gases represents all the C2-C6 light compounds; and finally, Coke that represents all the solid compounds formed due to thermal cracking reactions.

All the irreversible reactions from one heavy lump to a lighter one were considered to determine the number of reactions of the mechanism. However, according to Gianetto et al. [25], the contribution of the reaction to produce coke from gasoline in the concentration of coke and gasoline is low, hence, this reactions may be deleted from the mechanism. And conside-

ring that for FCC there is not a direct pathway to produce coke due to the cracking of the gases, this reaction also was deleted. Therefore, the mechanism for FCC is represented as shown in Figure 3-6. We can see the number of reactions for FCC that corresponds to eight kinetic parameters for its optimization.



**Figure 3-6.** Four-lumps FCC mechanism proposed in this thesis.

### 3.2.3. Modeling and equations

Unlike to hydrocracking process, the FCC process was simulated as a Plugged-Flow Reactor (PFR). The main assumption in the FCC process, catalyst particles and VGO are fluidized and the assumption that it is possible to simulate the process as a PFR reactor has been accepted. All the experimental data were simulated under the last process condition using PFR as a reactor model. We assume that the reactions rate follows an Arrhenius law and the model neglects any mass transfer restrictions and the reaction rates only involve the mass fraction of each lump. This approximation would be valid in the case where the catalyst deactivation was included in the kinetic constant. Also, this thesis considers lump-mechanisms could be represented as an implicit kinetic where each kinetic parameter includes the catalyst deactivation concentration as well as the mass transfer phenomena and the catalyst properties.

The system that represent the FCC is represented as a set of a second order reactions for VGO decomposition and first order reactions for gasoline or gas decomposition, also considering all of them are irreversible reactions. According to the mentioned above, the kinetic equation for FCC process will be as shown in the equations Eq. 3-7 and Eq. 3-8

$$\frac{dF_i}{dL} = \gamma_i \quad (\text{Eq. 3-7})$$

$$\gamma_i = k \times c_i^2 \quad (\text{Eq. 3-8})$$

The last equations only apply for the reactions corresponding to VGO decomposition which are second order reactions with the VGO composition during the process. And, the equations to calculate the velocity constants follow the Arrhenius expression as shown below in the equation Eq. 3-9.

$$k = A \times \text{Exp}\left(\frac{-E_a}{RT}\right) \quad (\text{Eq. 3-9})$$

In equation Eq. 3-9 we can see the exponential dependence of the kinetic parameters with the temperature.

To reduce this dependence, various studies, including that proposed by Blasetti and De Lasa [87] proposed a kinetic mechanism through a reparametrization of equation Eq. 3-9 to reduce the correlation between preexponential factors and activation energies. According equation Eq. 3-9, becomes:

$$k_{i,j} = A_{i,j} \text{exp}\left[\frac{-E_{i,j}}{R} \left(\frac{1}{T} - \frac{1}{T^{st}}\right)\right] \quad (\text{Eq. 3-10})$$

Using equation Eq. 3-10 instead of equation Eq. 3-9 may reduce the stiffness of the model. Therefore, the optimization could works better and find the local minimum easily. Unfortunately, this equation was only used for the FCC process due to limitations. However, it was demonstrated that better estimations can be obtained using the equation Eq. 3-10 as we can see in the Appendix D.

### 3.2.4. Kinetic Parameter Estimation

A total of 80 experimental data corresponding to eight different sources were taken into account to make a general fitting to get the best set of kinetic parameters for FCC process. It is necessary to know the lump-mechanism that will be used to represent this process.

After database was completed, *fmincon* routine from Matlab based on Levenberg-Marquardt algorithm was developed to estimate the corresponding kinetic parameters. The algorithm searches the optimal values that minimize the mean square error, MSE in equation Eq. 3-11, between experimental data and data obtained from this mechanism.

$$MSE = \sum_{i=1}^N (y_i^{pred} - y_i^{exp})^2 \quad (\text{Eq. 3-11})$$

Where N means the number of experimental data from the different sources, in this case, 80, Y represents yield, mass fraction or flows depending on the case, and  $y_i^{pred}$  and  $y_i^{exp}$  are the predicted and experimental yields for each lump in the mechanism respectively.

A weighting factor also was used in the FCC case due to the considerable differences between the lumps concentration along the riser reactor. It was demonstrated in the hydrocracking case that a weighting factor is successful to guarantee an equal optimization for each lump.

The same procedure to estimate the objective function for the FCC case was carried out. Hence, the objective function did not suffer a change for the kinetic parameter estimation for FCC. Therefore, the same minimization error function was also used as is shown in the equation Eq. 3-12 and equation Eq. 3-13

$$WSE = \sum_{i=1}^N w_i (y_i^{pred} - y_i^{exp})^{0.5} \quad (\text{Eq. 3-12})$$

and:



$$w_i = 1 / (y_i^{exp})^{0.5} \quad (\text{Eq. 3-13})$$

Despite using the same objective function for the FCC optimization, the steps to carry it out were different. The main difference for FCC case was the presetting of the kinetic parameters corresponding to the reaction 3 from the proposed mechanism for FCC. Given the importance of coke formation in catalyst deactivation, it was so important determine first that the mechanism fit as well as possible the coke formation for every experimental data. Therefore, considering that coke formation only depends from the VGO decomposition, one previous optimization was carried out optimizing the kinetic parameters related with coke formation regard coke experimental data. The obtained values were defined as initial values for the overall optimization. The another initial values were taken from one of the more recent mechanisms proposed by Dasila et al. [21].

### 3.3. Delayed Coking Process

In this section, a methodology to estimate the kinetic parameter for Delayed Coking is developed. It is to important to point out the similarities between the Delayed Coking and Hydrocracking in the way how the experiments were carried out. It means that, according to the data from literature related with delayed coking. It will be explain further in the subsection Modeling and equations.

#### 3.3.1. XML (eXtensible Mark-Up Language) data standardization

The number of available data for delayed coking is less than the other process mentioned above. One of the main reasons is the process is the more recent. Although there are a several researches about cracking processes, the interesting of delayed coking process just start in the last decades. However, a set of experimental data were collected to give a global vision of the delayed coking as we proposed for the last processes.

The methodology was identical to described before. Taking into account that all the experiments to get the experimental data collected in this research were carried out in batch reactors, therefore, the experimental data collected in the XML database has associated only

two process conditions, as it have been see for hydrocracking process, the process conditions are temperature and residence time, this was LHSV for hydrocracking. The process conditions which were collected through experimental data were in the range of 410 and 475 ° C for the temperature and one and two hours for the residence time.

A total of 32 data corresponding to three different authors were collected to make the optimization. It is expected that the set of experimental data may enough to give a global vision about the delayed coking process.

### 3.3.2. Modeling and equations

The DC process was simulated as a Batch Reactor. Considering all the experiments worked at isothermal conditions, the set of reactions could be represented as shown in the Eq. 3-14

The system that represent the Delayed Coking is represented as a set of a second order reactions for VGO decomposition and first order reactions for de gasoline or gas decomposition, also considering all of them are irreversible reactions. According to the mentioned above, the kinetic equation for DC process will be as shown in the Eq. 3-14

$$\frac{dc_i}{dt} = \gamma_i \quad (\text{Eq. 3-14})$$

Because of all reactions are first order reactions, the equations to calculate the velocity constants are the same and follow the Arrhenius expression. This equations are shown below (Eq. 3-15).

$$k = A \times \text{Exp} \left( \frac{-E_a}{RT} \right) \quad (\text{Eq. 3-15})$$

### 3.3.3. Kinetic Parameter Estimation

A total of 32 experimental data corresponding to four different sources were taking into account to make a general fitting to get the best set of kinetic parameters for Delayed coking

but first, it is necessary to know the lump-mechanism that will be used to represent this process.

After database was completed, *fmincon* routine from Matlab based on Levenberg-Marquardt algorithm was developed to estimate the corresponding kinetic parameters. The algorithm search the optimal values that minimizes the mean square error, MSE in equation Eq. 3-16, between experimental data and data obtaining from this mechanism.

$$MSE = \sum_{i=1}^N (y_i^{pred} - y_i^{exp})^2 \quad (\text{Eq. 3-16})$$

Where N mean the number of experimental data from the different sources, in this case, 32, Y represents yield, mass fraction or flows depending on the case, and  $y_i^{pred}$  and  $y_i^{exp}$  are the predicted and experimental yields for each lump in the mechanism respectively.

A weighting factor also as used in the DC case due to the considerable differences between the lumps concentration along the riser reactor. It was demonstrated in the hydrocracking case that a weighting factor is successful to guarantee an equal optimization for each lump.

The same procedure to estimate the objective function for the FCC case was carried out. Hence, the objective function did not suffered a change for the kinetic parameter estimation for FCC. Therefore, the same minimization error function was also used as is shown in the Eq. 3-17 and Eq. 3-18

$$WSE = \sum_{i=1}^N w_i (y_i^{pred} - y_i^{exp})^{0.5} \quad (\text{Eq. 3-17})$$

and:

$$w_i = 1 / (y_i^{exp})^{0.5} \quad (\text{Eq. 3-18})$$

## 4. Results and Analysis

This chapter presents the main results of this thesis. Following the methodology from Chapter 3, The thesis presents the results when it was applied to each process: HC, FCC and DC. The XML representation of the experimental data for each process is in the Appendix E and also available in the FRUN web page [88]. The chapter also shows the selected lump-mechanism for each process and the corresponding kinetic parameter estimation and uncertainty calculation. Finally, each mechanism was validated with experimental data taken from literature. This chapter also explains the compensation effect between kinetic parameters from the same reaction.

### 4.1. Hydrocracking

#### 4.1.1. Data compilation

In order to get a kinetic mechanism based on the existing experimental literature for the catalytic HC process, a total of 99 points corresponding to six different [13–16] authors were taking into account for the creation of the database. XML structure has been widely used given its multiple advantages.

For HC process the gathered data allow us to perform the analysis in a range of conditions wider than usually reported in literature. For temperature, the range of working of the general mechanism was between 360°C and 450°C, and 0.8 h<sup>-1</sup> and 1.5 h<sup>-1</sup> for the Liquid Hourly Space velocity (LHSV). Most of reported studies works only with one kind of VGO, even (380°C-400°C) and 1 h<sup>-1</sup> and 1.2 h<sup>-1</sup>.

Despite the XML database, as show in the appendix E, includes more than 10 works, only a few of the works published experimental data for lumps which properties could be calculated,

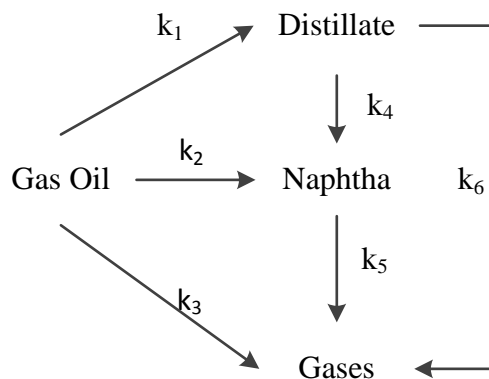
therefore, these were chosen for the model validation. Another works such as the developed by Botchew et al. [15] that consider different lumps than the mechanism proposed here, was included due to consider also a VGO decomposition, hence, only data regarding for VGO decomposition were used for validation.

On the other hand, given that Aboul-gheit [13] proposed a lump-mechanism for hydrocracking and according to Martinez et al. [12] agree that the model had a fitting coefficient near to 1, simulations were carried out under typical conditions in order to generate the experimental data for further validation with this mechanism.

## 4.1.2. Optimization and uncertainty calculation

### 4.1.2.1. Optimization routine

Figure 4-1 shows the total number of lumps and reactions for the mechanism. As explained in Chapter 3, it was assumed that the reaction rate constant could be represented by an Arrhenius expression which implies the estimation of 12 kinetic parameters for the mechanism selected to represent the HC process.



**Figure 4-1.** Four-lumps HC mechanism proposed in this thesis.

Table 4-1 shows the set of kinetic parameters for the HC process that was obtained using

the *fmincon* routine as explained in the last chapter.

**Table 4-1.** Uncertainty values for each kinetic parameter obtained from the bootstrap technique

Reaction	Ln Ko(g/gcat.h)	Uncertainty value
1	10.1277	0.5119
2	27.9983	0.7786
3	19.2296	0.3823
4	5.5026	0.98207
5	3.7916	0.4904
6	24.0114	0.0631

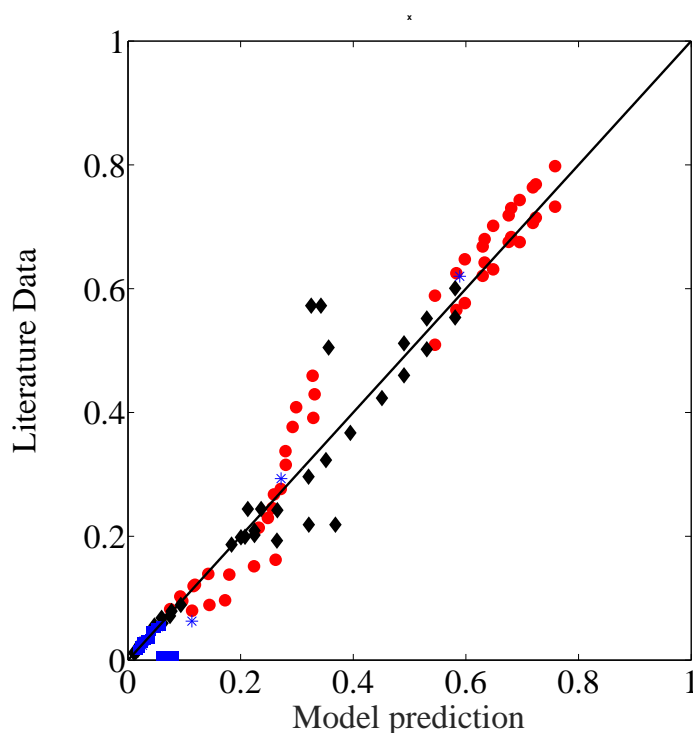
Reaction	Ea(kJ/mol)	Uncertainty value
1	59.7720	2.7807
2	213.9262	0.2161
3	216.9726	0.1633
4	33.0237	5.2053
5	31.7994	2.6528
6	281.8131	1.0545

Table 4-1 shows non typical values for the kinetic parameters corresponding to the reactions 3 and 4. Despite model have a good fit with the experimental data, values for  $Ea_3$  and  $Ea_4$  are low taking into account that for cracking reactions the values are bigger. Also, we have to take into account that these values correspond to global pathways between pseudo components and the empiricism associated with the optimization method leads to obtain low values in the kinetic parameters as we observed for  $Ea_3$  and  $Ea_4$ .

To asses the goodness of the kinetic parameters to fit the experimental data, Figure 4-2 shows a parity plot that relates the model results and the data collected. Most of the points are close to the parity line. The estimated value of  $R^2$  is 0.96, an acceptable value given the differences in the sources of experimental data. However, The model has a regular fitting with some data at high temperatures (black diamonds and blue squares) proposed by [14,15]. Despite this regular fitting at 450°C, we can also see the good fitting with the experimental data which were included as blue asterisks.

Despite the fact that Figure 4-2 indicates a good fitting of the proposed mechanism, an additional sensitivity analysis was carried out by changing one parameter at a time in a

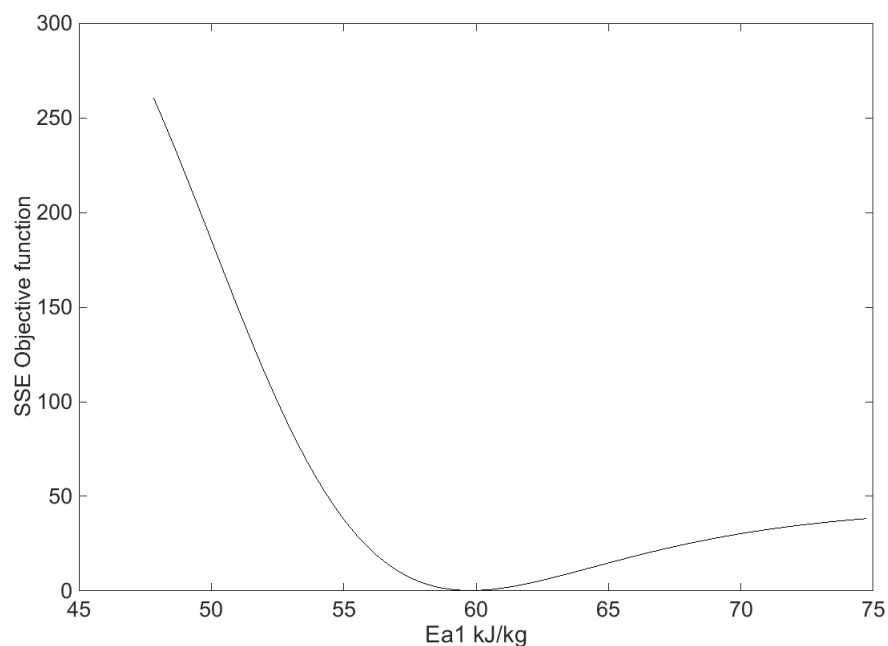
specified range, and then recalculating the objective function. By observing the changes in the objective function, one can determine if the obtained solution was indeed a minimum of the objective function.



**Figure 4-2.** Parity plot for the model prediction and data taken from literature. Red dots [14], black squares [13,15], Blue dots [16].

Figure 4-3 shows the sensitivity of the objective function to the activation energy of reaction 1. In Figure 4-3 the existence of a local minimum, at the estimated  $E_a$  corresponding to the reaction 1, is evident. The X axis represent the ratio between the value of the parameter and the optimized value, therefore, number 1 in the X axis represent the optimized value obtained in the previous step. The same analysis for all the parameters is available in Appendix A. In all cases the presence of a local minimum was evident.

As final test for the kinetics that resulted from the optimization process, Figure 4-4 compares the model predictions to that of the experimental data reported by Mohanty et al. [17]. The figure shows that, although not perfect, the experimental data with an absolute error less than 10%.



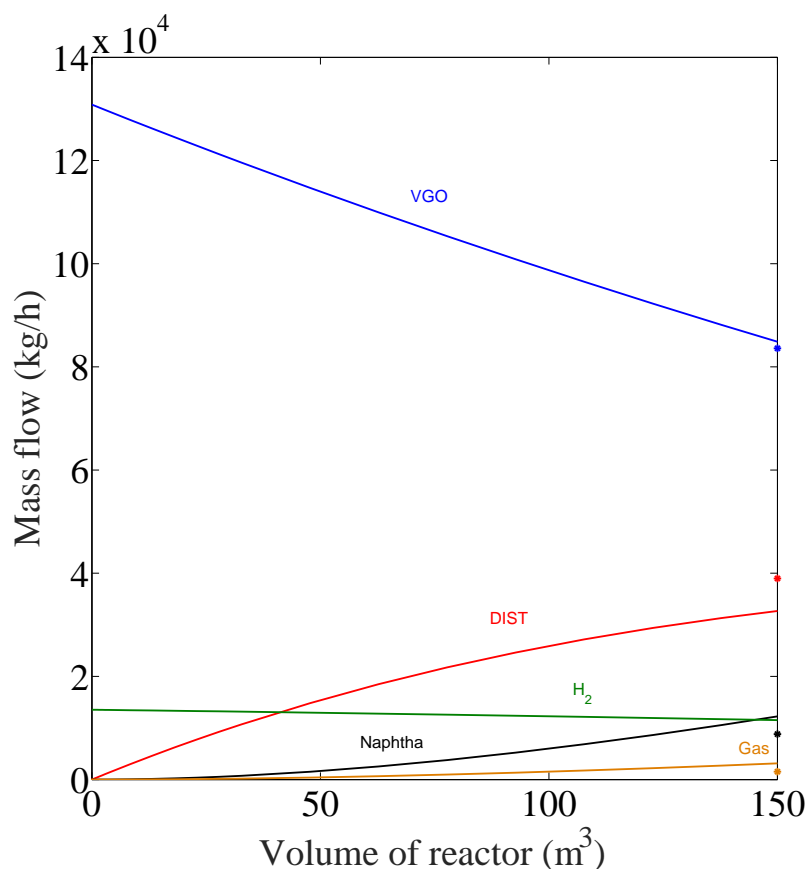
**Figure 4-3.** Sensitivity of the objective function to variations in the activation energy of the reaction 1 of the mechanism in Figure 4-1

#### 4.1.2.2. Uncertainty calculations

The bootstrapping technique, as it was described in the Chapter 3, is a powerful Monte Carlo (MC) method to determine the uncertainty of a parameter determination process when the data set is small or not enough to know the distribution through re-sampling of the original set of data, keeping the same size of this. Table 4-1 shows the uncertainty values corresponding to each parameter of the HC mechanism.

In general the uncertainty values are very low and tend to be less than 10 % of each parameter. As mentioned in Chapter 3, it is important to remember that uncertainty is associated to the parameter estimation process as it does not consider any experimental errors. Figure 4-5 shows that care was taken to guarantee that the number of bootstrap samples was enough to guarantee a good representation of the kinetic parameters. Similar plots are available for the pre exponential factors in Appendix A. Figure 4-7 presents an example of the histogram of different values that result from the multiple optimizations that take place during the bootstrap process. The figure only shows results for reaction 1, but similar plots are available



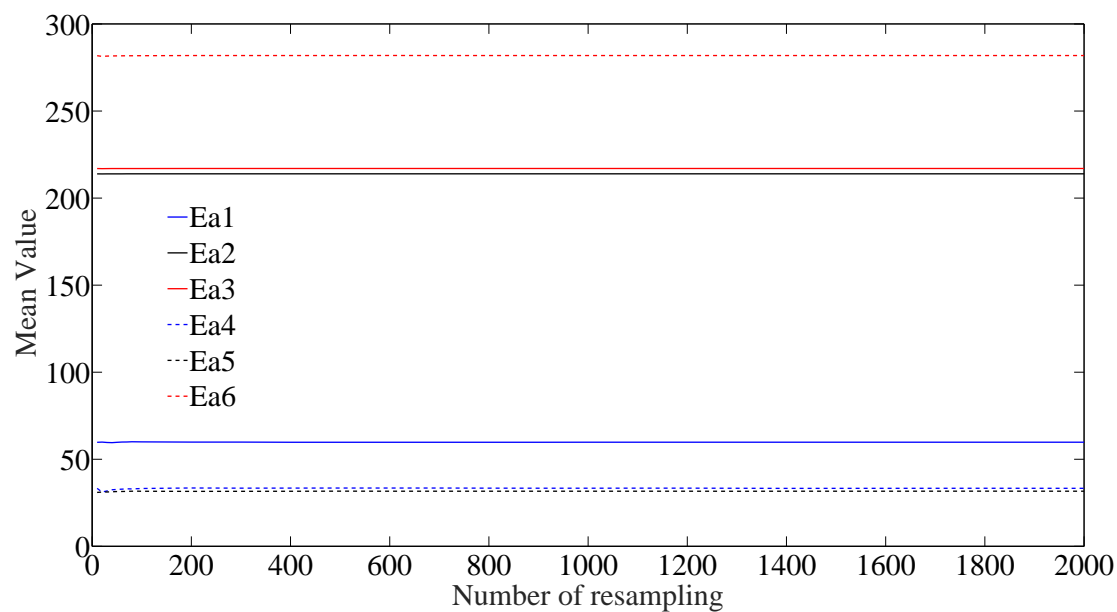


**Figure 4-4.** Comparison between experimental in reference [17] for HC of an oil fraction and the model using the parameters in the Table 4-1.

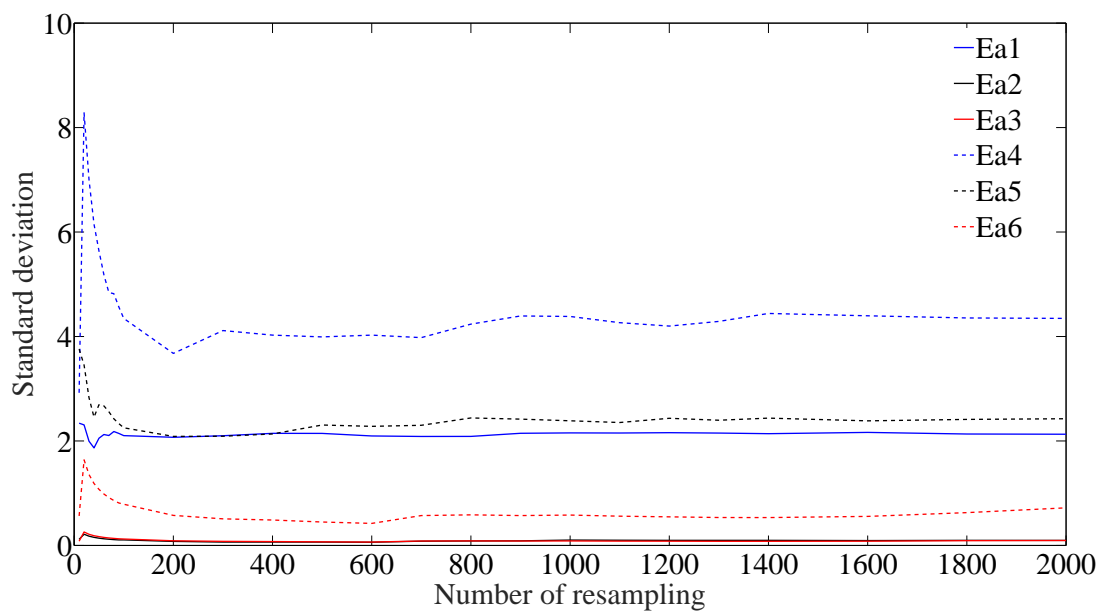
for all other parameters in Appendix A. The fact that the distribution tends to be centered at the optimized parameter gives confidence that the uncertainty and parameter estimation calculations are correct.

Figure 4-5 shows the results obtained from the tested of how change the values for the mean of the re samples bootstrapp. The figure also show that the values for each energy activation is stable with the resampling. Given that the value of each energy activation does not represent a significance change, we need to follow this methodology to make the same analysis with the standard deviation.

Figure 4-6 shows the results obtained from the tested of how change the values for the standard deviation of the re samples bootstrapp. Unlike the Figure 4-5, this Figure presents more changes with the bootstrapping resamples. We can observed the big changes associated

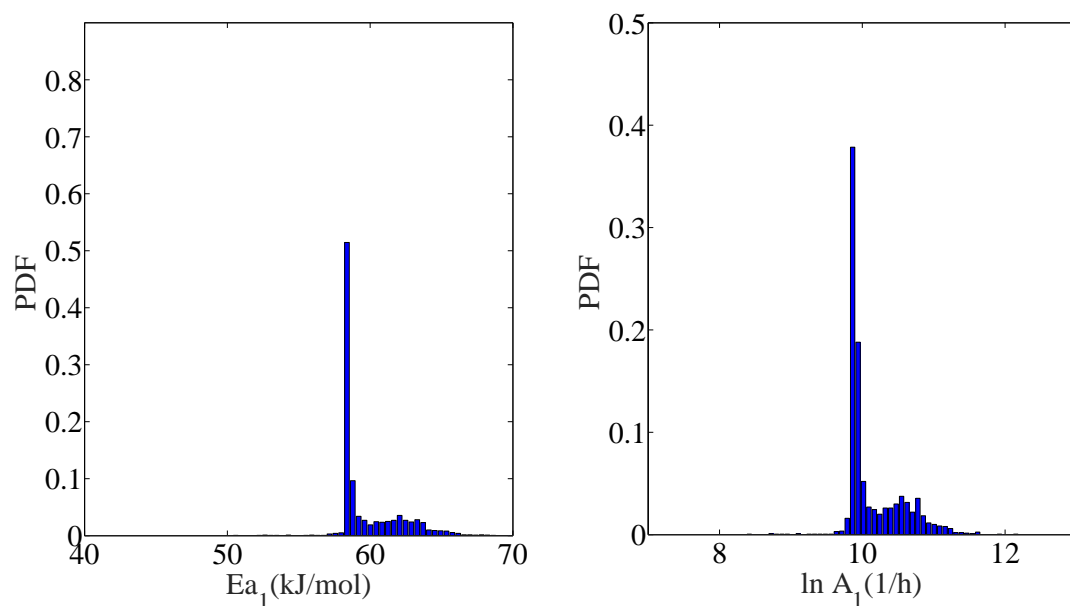


**Figure 4-5.** Variation of the activation energies with respect to number of bootstrap resampling



**Figure 4-6.** Variation of the standard deviation of activation energies with respect to number of bootstrap resampling

with the  $E_{a_4}$  in the first 300 iterations, and after between iteration 1000 and 1400. Despite using 2000 bootstrapp resampling, the Figure 4-6 shows that 1600 iterations would have been enough to estimate the kinetic parameters for HC where the standard deviation values for each kinetic parameter are established. The same analysis was carried out for the pre exponential factor. The results, in the appendix A, also shows that 2000 bootstrapp resampling are enough to calculate the kinetic parameter for HC.



**Figure 4-7.** Histogram distribution for the activation energy corresponding to reaction 1 for HC mechanism

Figure 4-8 shows the compensation effect between the kinetic parameters corresponding for reaction 3 and 4 from the HC mechanism. Figure also shows that despite the correlation shows a more dense zone close to the optimized values, which are the expected results, the linear behavior is highly predominant for HC. Given the background in the Chapter 3, the linear behavior corresponds mainly because all of the reactions for HC are first-order reactions.

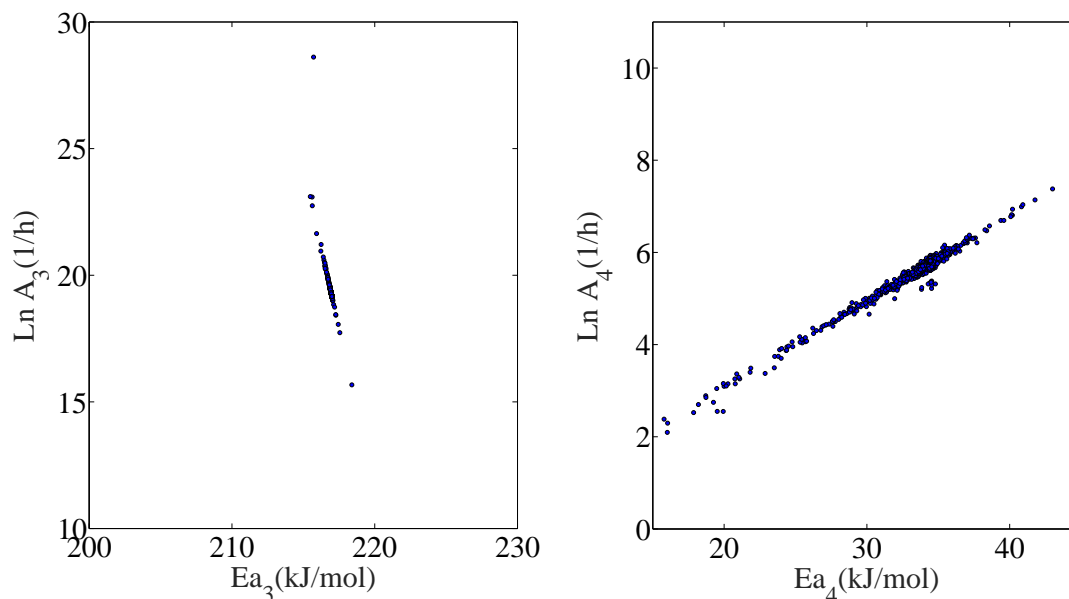


Figure 4-8. Scatter distribution for the kinetic parameters for the reactions 3 and 4

## 4.2. Fluid Catalytic Cracking

### 4.2.1. Data compilation

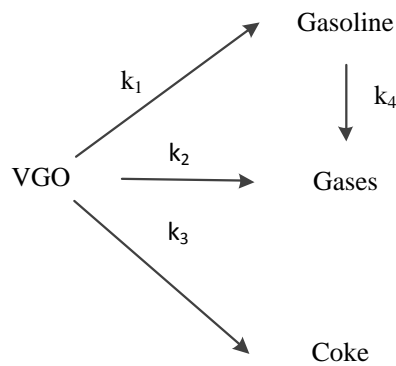
The XML database for FCC contains the main process conditions such as initial mass flow rate of VGO, temperature of reactor, molecular weight of lumps, catalyst oil ratio, length of reactor, and yields of each lumps at the exit of the reactor. For a better understanding of the database, a tree-structure XML was used to represent the experimental data associated with FCC. The XML database is in the appendix F and also available in the FRUN web page [88].

### 4.2.2. Optimization and uncertainty calculation

#### 4.2.2.1. Optimization routine

Chapter 3 showed the equations to carry out the optimization process. With a complete database, a four-lump mechanism for FCC process was proposed. Figure 4-9 shows the total

number of lumps and reactions for the mechanism.



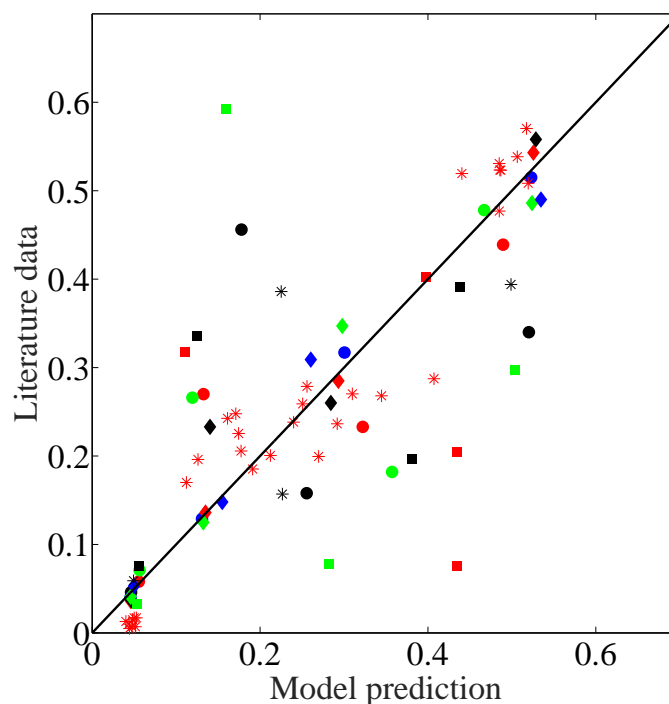
**Figure 4-9.** Four-lumps FCC mechanism proposed in this thesis.

For the FCC case, the products were lumped according to its molecular structure. VGO considers compounds between 19 and 22 carbon atoms, Gasoline ( $C_3$ - $C_{12}$ ), light gases ( $C_2$ - $C_6$ ) and coke as a solid product of the cracking reactions. For the mechanism described before, each velocity constant follows the Arrhenius expression which leads to estimate eight kinetic parameters for the FCC mechanism.

Once again, this work used optimization *fmincon* routine available in Matlab 2014 to minimize the objective function and obtain the kinetic parameters. The kinetic parameters obtained after the optimization process guarantee an acceptable agreement between model and experimental data as the parity plot in Figure 4-10 shows. Although the points in the figure are more scattered than the HC results, ( $R^2$  for the FCC parity plot was 0.62 while that for HC was 0.94), they follow the tendency of the perfect parity (line) including the experimental data taken from Gianetto et al. [25] marked as red asterisks, and experimental data from an industrial riser marked as black asterisk.

Table 4-2 shows the values of the kinetic parameters using the *fmincon* routine and the objective function previously defined in the chapter 3. In general the uncertainty values are very low and tend to be less than 10% of each parameter.

According to Figure 4-11, the values obtained in the optimization correspond to a minimum value in the objective function when the pre exponential factor for reaction 1 changed in

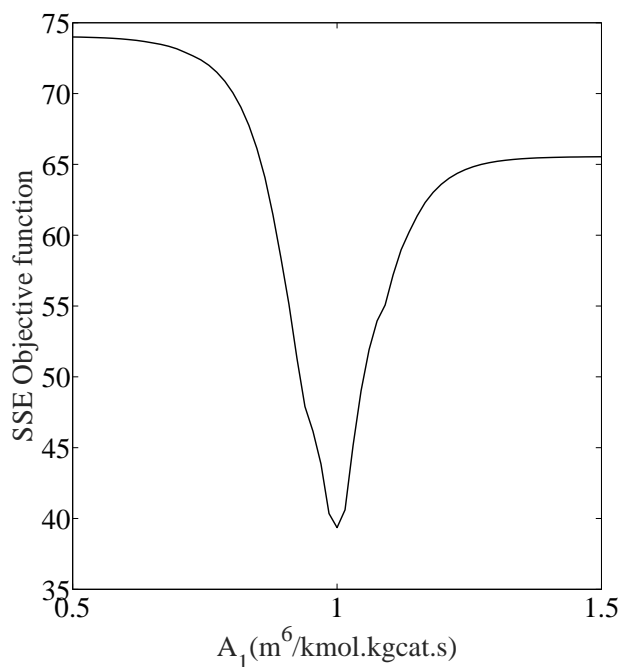


**Figure 4-10.** Parity plot for the model prediction and data taken from literature [18–25]

**Table 4-2.** Uncertainty values for each kinetic parameter obtained from the bootstrap technique for the proposed mechanism for FCC

Reaction	Ln Ko(m <sup>6</sup> /kmol.kgcat.s)	Uncertainty value
1	14.411	0.9041
2	12.555	0.8874
3	10.134	0.971
Reaction	Ln Ko(m <sup>3</sup> /kgcat.s)	Uncertainty value
4	6.225	1.638
Reaction	Ea(kJ/mol)	Uncertainty value
1	89.101	1.7829
2	84.508	2.046
3	71.616	2.7091
4	80.703	0.7664

50 %. A similar analysis for the other parameters yields the same evidence of the existence of a local minimum as shown in Appendix B.

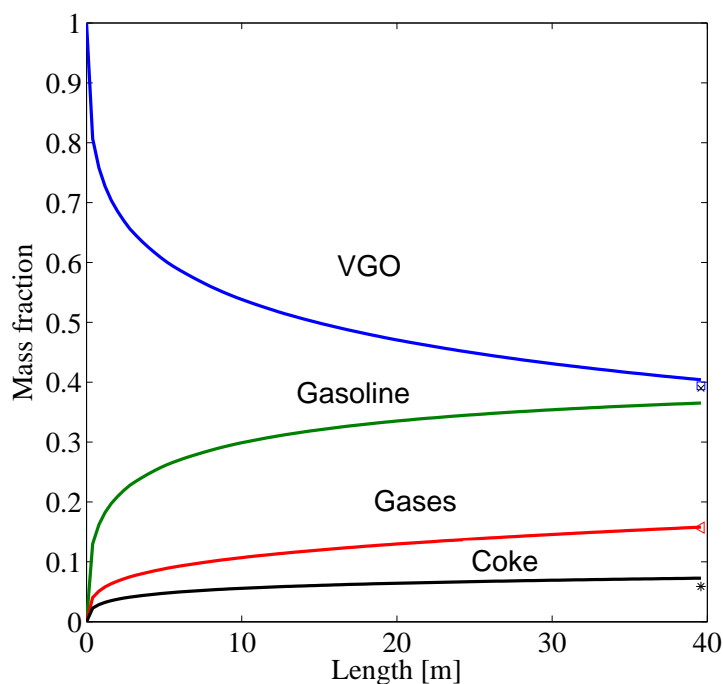


**Figure 4-11.** Sensitivity for activation energy of the reaction 1 of the proposed mechanism for FCC

The evaluation of the parameters showed in Table 4-2 used this parameters in a model of an industrial riser reactor in order to determine how the proposed mechanism can represent experimental data from a local refinery. These data were not included in the database. Figure 4.2.2.1 also shows a good fitting between the model and experimental data.

#### 4.2.2.2. Uncertainty calculations

Following the same procedure than the applied to calculate the uncertainty values for HC process. Table 4-2 shows the uncertainty values corresponding to each parameter of the FCC mechanism. In general the uncertainty values are also very low and tend to be less than 10 % of each parameter. As mentioned in Chapter 3, it is important to remember that uncertainty is associated to the parameter estimation process as it does not consider any experimental errors. Figure 4-13 shows that care was taken to guarantee that the number of bootstrap samples was enough to guarantee a good representation of the kinetic parameters. Similar plots are available for the pre exponential factors in Appendix A. Figure 4-15 presents an



**Figure 4-12.** Representation of the experimental data for FCC Industrial riser using the parameters in Table 4-2

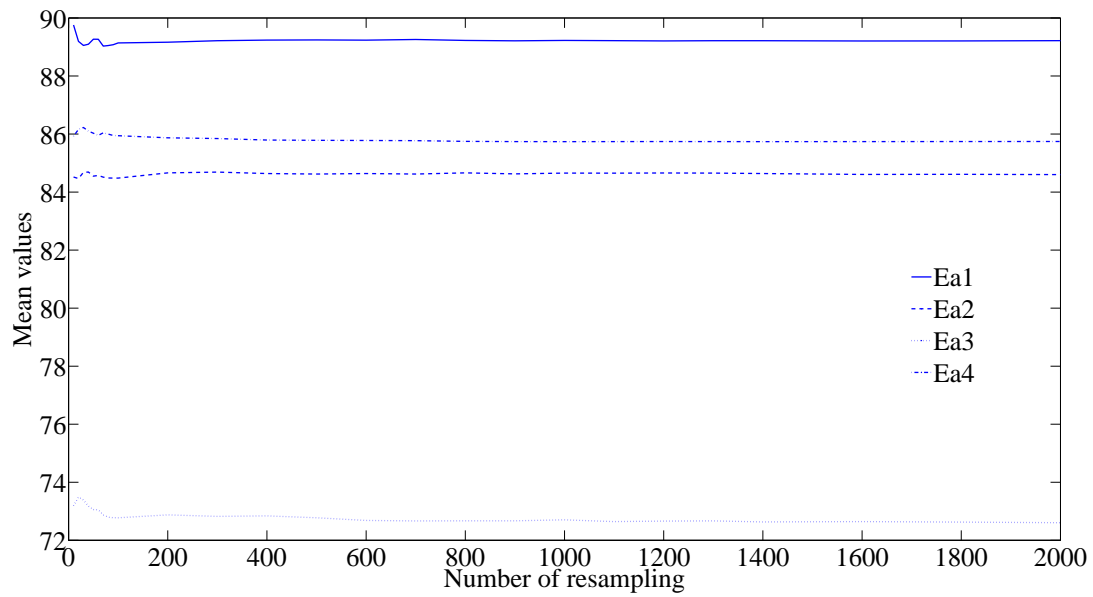
example of the histogram of different values that result from the multiple optimizations that take place during the bootstrap process. The figure only shows results for reaction 1, but similar plots are available for all other parameters in Appendix B. The fact that the distribution tends to be centered at the optimized parameter gives confidence that the uncertainty and parameter estimation calculations are correct.

Similarly to HC, we developed an analysis based upon the changes in the values of standard deviation for the activation energies and pre exponential factors. Figure 4-14 shows these changes for the activation energy values. In the initial 600 iterations we can see that the values of keep unstables, and even the value for  $E_{a1}$  between 1000 and 1200 iterations presents considerable changes. The values established from the iteration 1600.

The Figure 4-15 show the distribution for the reaction that transforms VGO gasoline. The others histograms are in Appendix B.

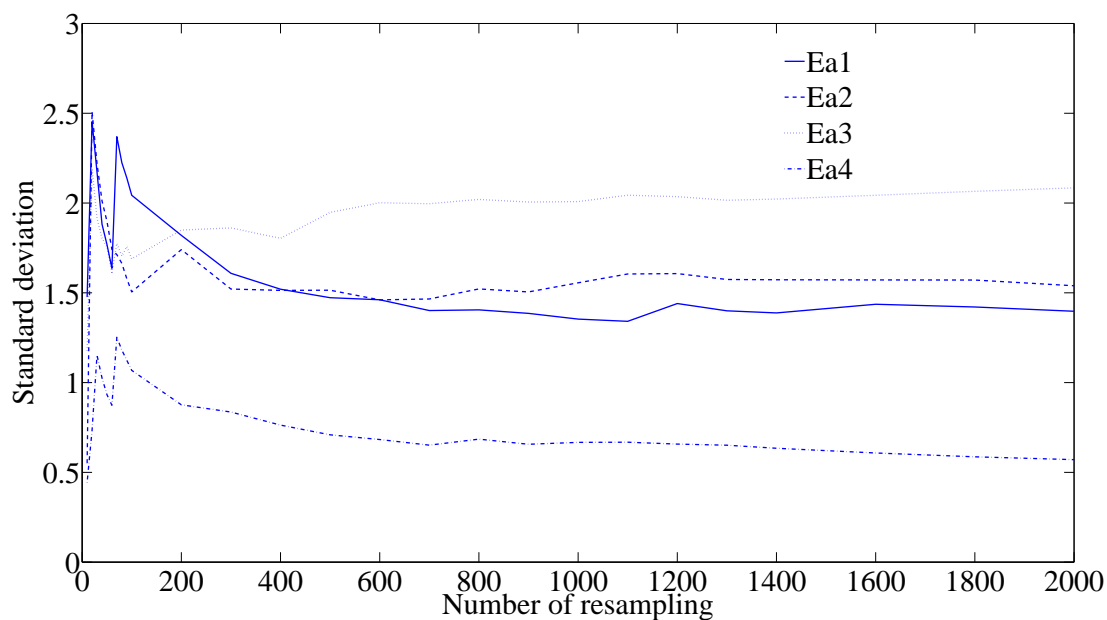
To determine the optimum number of re sampling bootstrap it was necessary to quantify



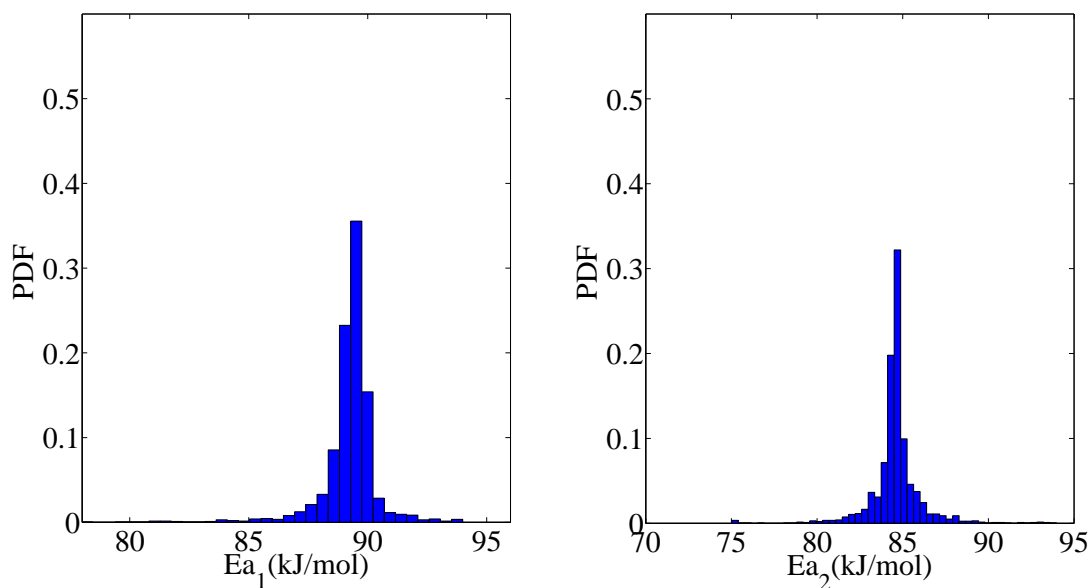


**Figure 4-13.** Variation of the activation energies with respect to number of bootstrap re-sampling

how change the mean values and standard deviation of each parameter with the number of bootstrap, and after to define the number of bootstrap for this process. Figure 4-13 shows how to change the activation energy of the re sampling with the number of re sampling.

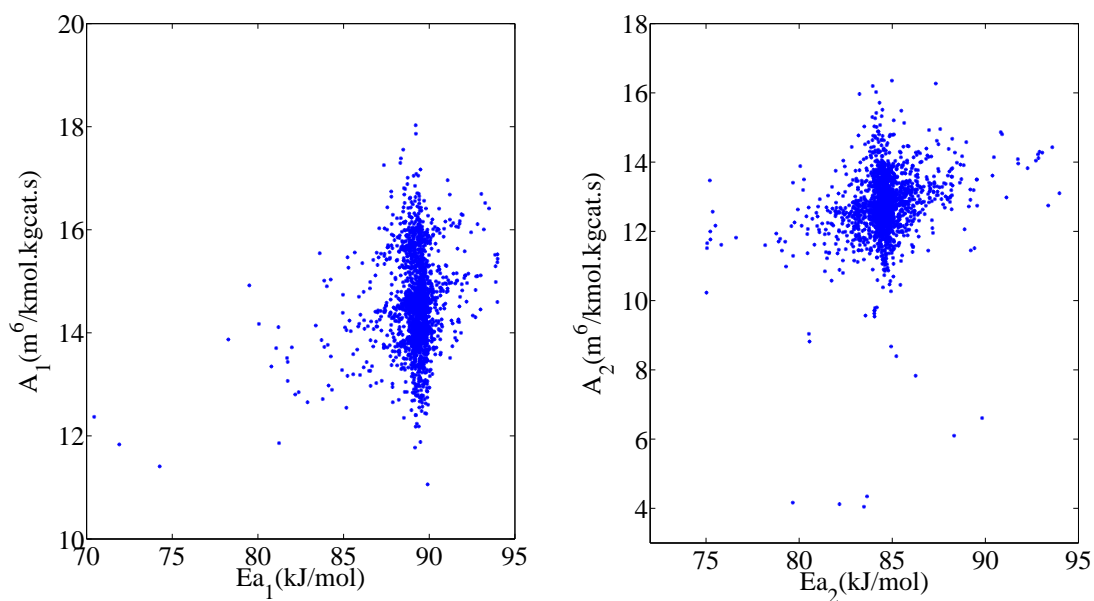


**Figure 4-14.** Variation of the standard deviation for activation energies with respect to number of bootstrap resampling



**Figure 4-15.** histogram distribution for kinetic parameter corresponding to reactions 1 and 2

Figure 4-16 shows the distribution of the results as a scatter plot. This plot shows the region where is more likely to find the set of kinetic parameters. The other distributions are in the appendix B. Also, Figure 4-16 indicates that the compensation effect is not present in the FCC optimization. The reason for may stem from the fact that most reactions are second order. As explained above, first-order reactions are more prone to suffer the compensation effect.



**Figure 4-16.** Scatter distribution for the kinetic parameters for the reaction 3

## 4.3. Delayed Coking

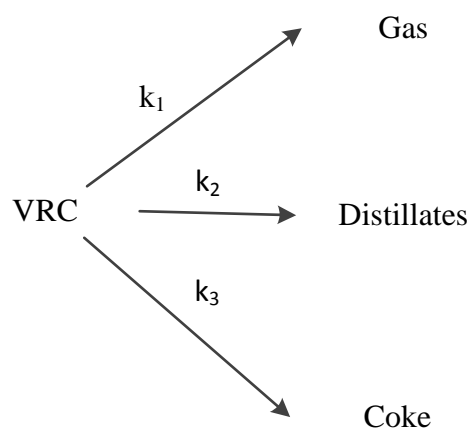
### 4.3.1. Data compilation

The XML database for DC process contains the main conditions for batch reactors, given that all the experiments reviewed were carried out in this kind of reactor. Therefore, the XML database has only residence times and temperature. For a better understanding of the database, a tree-structure XML was used to represent the experimental data associated with DC. The XML database is in the appendix G and also available in the FRUN web page [88].

### 4.3.2. Optimization and uncertainty calculation

#### 4.3.2.1. Optimization routine

Based upon equations from Chapter 3 to describe the DC process, one mechanism that includes the most representative lumps for this process was proposed here. Figure 4-17

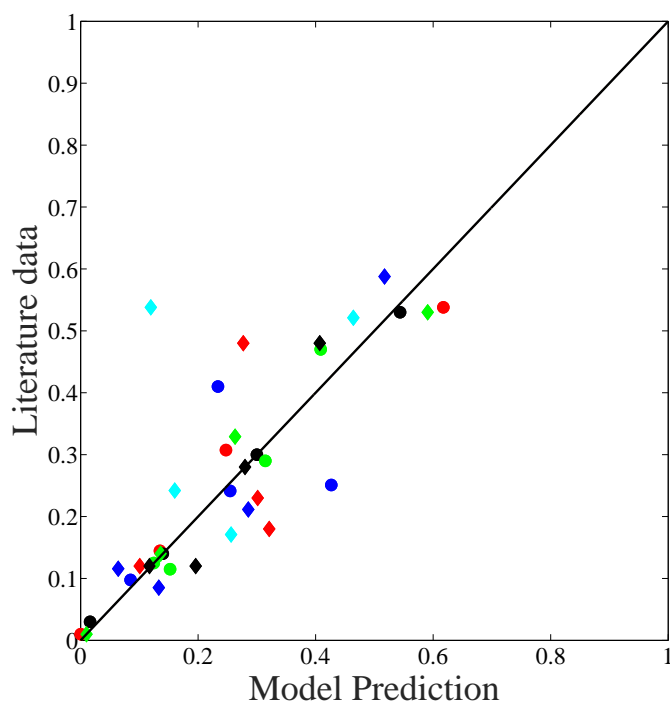


**Figure 4-17.** Four-lumps DC mechanism proposed in this thesis.

For the DC case, the mechanism proposed in this thesis agrees with other reported studies in the classification of pseudo-components (VRC, gases, distillates and coke) and the number of

lumps. VRC, gases, distillates and coke. For the mechanism described before, each velocity constant follows the Arrhenius expression which leads to estimate six kinetic parameters.

We followed the same optimization process described in HC and FCC sections and a similar objective function define in Chapter 3. We found that the model's results have a good fitting with the experimental data, as shown in Figure 4-18 with relative good agreement ( $R^2=0.94$ ) shows a parity plot between data obtained from our model and the data taken from literature.



**Figure 4-18.** Parity plot for the model prediction and data taken from literature.

The table 4-3 shows the values of the kinetic parameters obtaining using the *fmincon* routine and the objective function previously defined in Chapter 3.

The same procedure was followed to carry out the sensitivity analysis described in previous sections. As an example Figure 4-19 shows the behavior of the objective function when we change the parameters corresponding to the reaction that transform VRC in gases. We conclude that the optimization was successful and that the obtained parameters are local minima optimum. Thus, we accept these values as the kinetic parameters for the DC process.

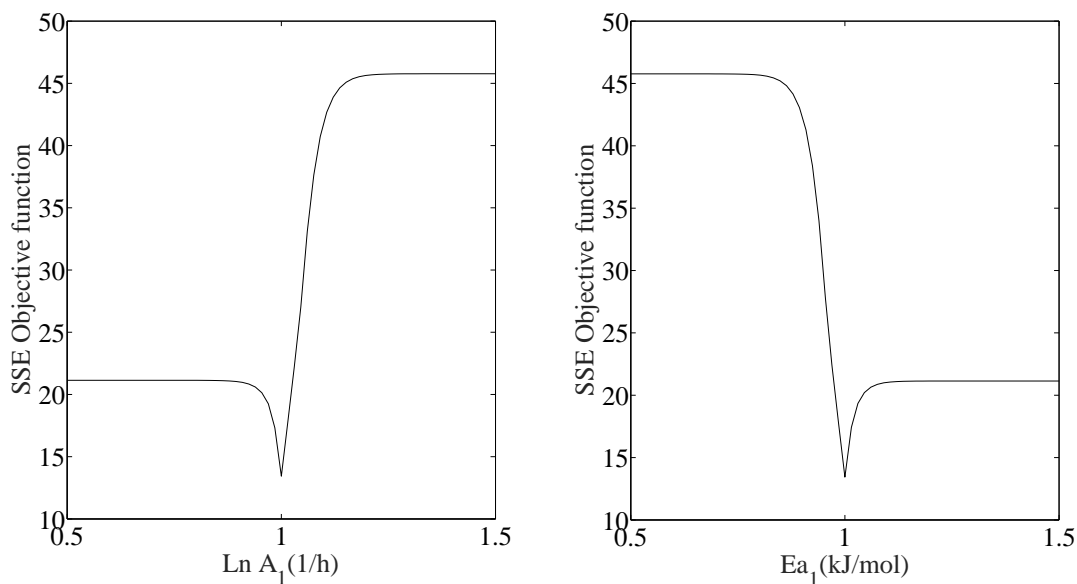
Figure 4-19 shows a symmetrical values in the objective function with a change in the pa-

**Table 4-3.** Uncertainty values for each kinetic parameter obtained from the bootstrapp technique

Reaction	Ln Ko(1/h)	Uncertainty value
1	34.90	0.51
2	27.78	0.85
3	44.06	1.00

Reaction	Ea(kJ/mol)	Uncertainty value
1	219.71	2.64
2	171.73	5.03
3	268.02	5.80

**Figure 4-19.** Sensitivity for activation energy of the reaction 1 of the proposed mechanism for DC

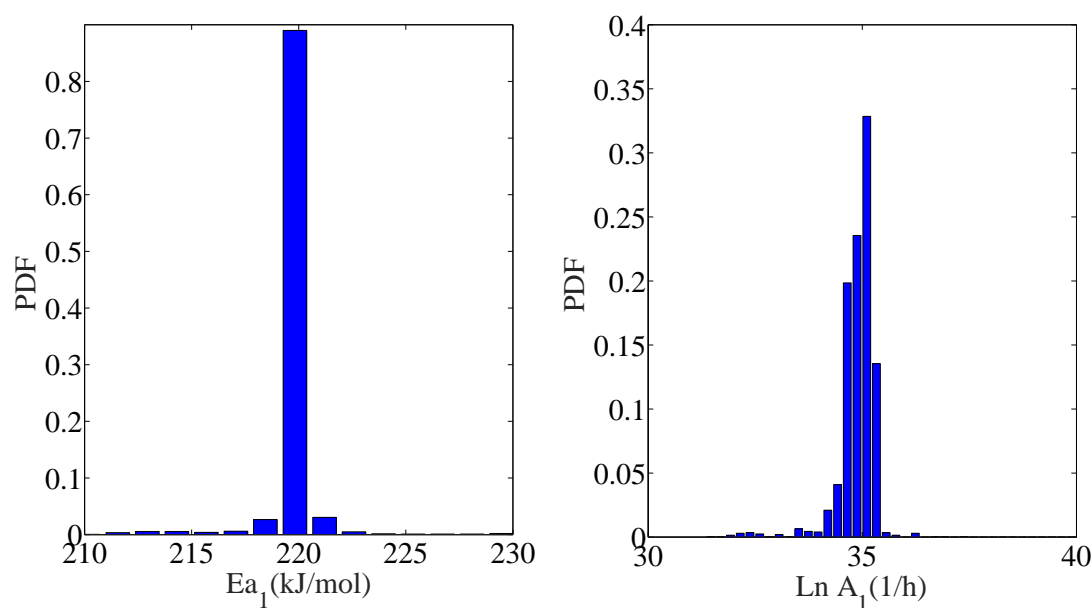
rameters from the same reaction for DC. In this case, Figure 4-19 shows the corresponding parameters for reaction 1. The symmetric behavior follow the compensation effect phenomenon. Given that activation energies and pre exponential factors are strongly coupled, it is reflected in the figure above. Figure 4-19 also shows objective function trends to be constant when the variation is over 1.5 times the minimum value. This behavior occur for every reac-

tion for DC (Appendix C) due to extreme values for each kinetic parameter, it means that, for instance, in the case of  $E_{a_1}$  lower values (0.5 times of optimized value), decomposition of VRC will take place instantaneously and implies the highest error against experimental data. In the other side, if the value of  $E_{a_1}$  is extremely high, VRC will not decompose and implies another high error. The same analysis could be carried out for  $A_1$ .

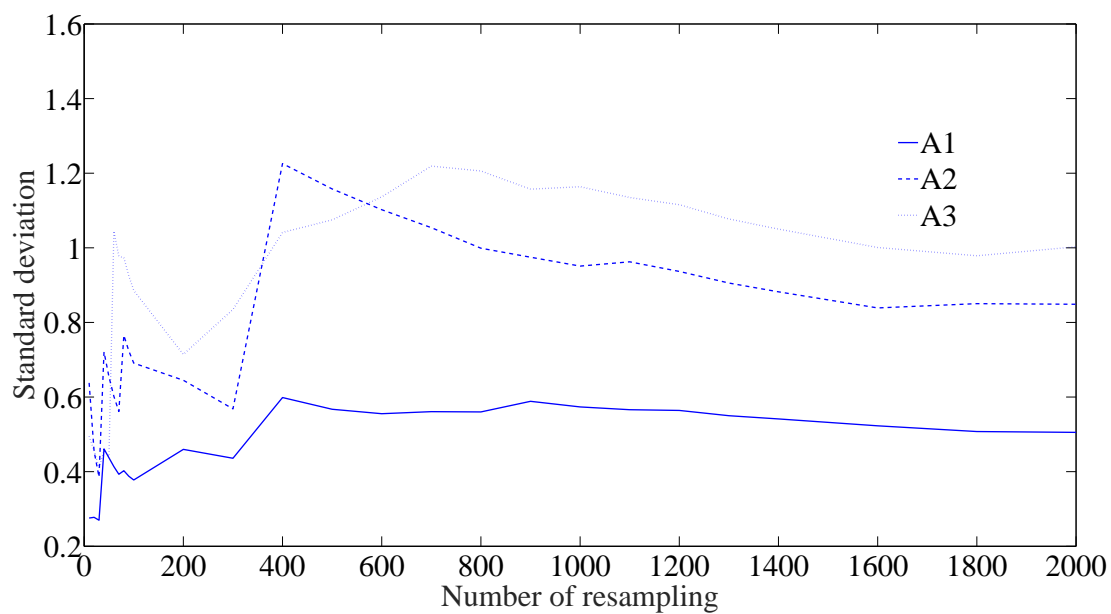
#### 4.3.2.2. Uncertainty calculations

Finally, we followed the bootstrap methodology for generating 2000 sets of parameters and analyze their distribution and standard deviation. Table 4-3 shows the uncertainty values corresponding to each parameter of the DC mechanism. The DC results can show the same results as distribution probability diagram or using histograms that enable to see clearly the distribution of each kinetic parameter. The figures below Figure 4-20 show this distribution for the kinetic parameters corresponding to DC process. The others histograms are in the appendix C.

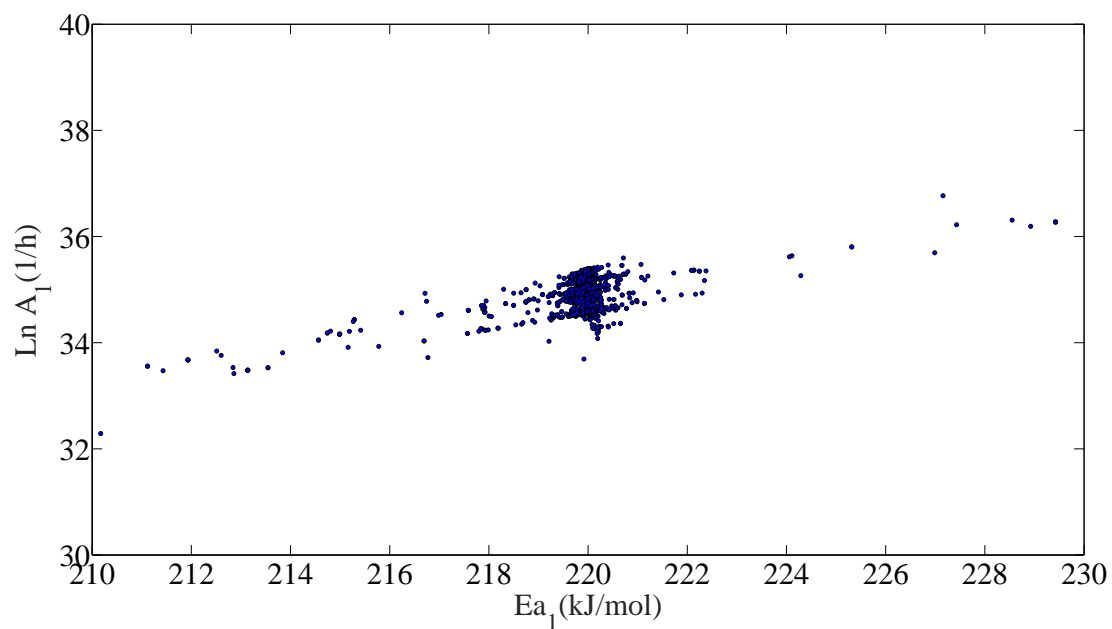
Finally, Figure 4-22 presents the scatter plot of the most probable region for the kinetic parameters. We observed the same behavior than HC process. It is mainly because DC has first-order and irreversible reactions.



**Figure 4-20.** Histogram distribution for kinetic parameter corresponding to reaction 1



**Figure 4-21.** Variation of the activation energies with respect to number of bootstrap re sampling



**Figure 4-22.** Scatter distribution for the kinetic parameters for DC for the reaction 1



## 5. Conclusions

This thesis developed a lump kinetic model for three important refinery processes: Hydrocracking, Fluid Catalytic Cracking and Delayed Coking. We used XML for compiling, storing and unifying experimental data reported in literature for the three processes. By using the *fmincon* routine from Matlab, it was possible to calculate the best set of kinetic parameter for each lump kinetic model obtaining a good fitting with the data. The soundness of the kinetic model was ensured by a sensitivity analysis for the calculation of each set of kinetic parameters and the adaptation of a powerful statistic technique for the calculation of the uncertainty associated with each parameter. The bootstrap technique is a tool for calculating uncertainty when the uncertainties associated to experimental data are not available, like in our case.

This thesis provides a tool for developing lump kinetic models when experiments are not available. We highlight that the best way to get a lump kinetic model is through experimentation, as this way we can obtain kinetic parameters for the exact process conditions (feedstock, residence times, temperature, pressures, etc). However, the goal of this thesis was to give a more global approach than the traditional alternative to experiments that the CFD community normally takes, i.e. the selection of the kinetic expressions available in just one scientific publication. The use of the XML standardization and the optimization and uncertainty analysis described above provide this alternative.

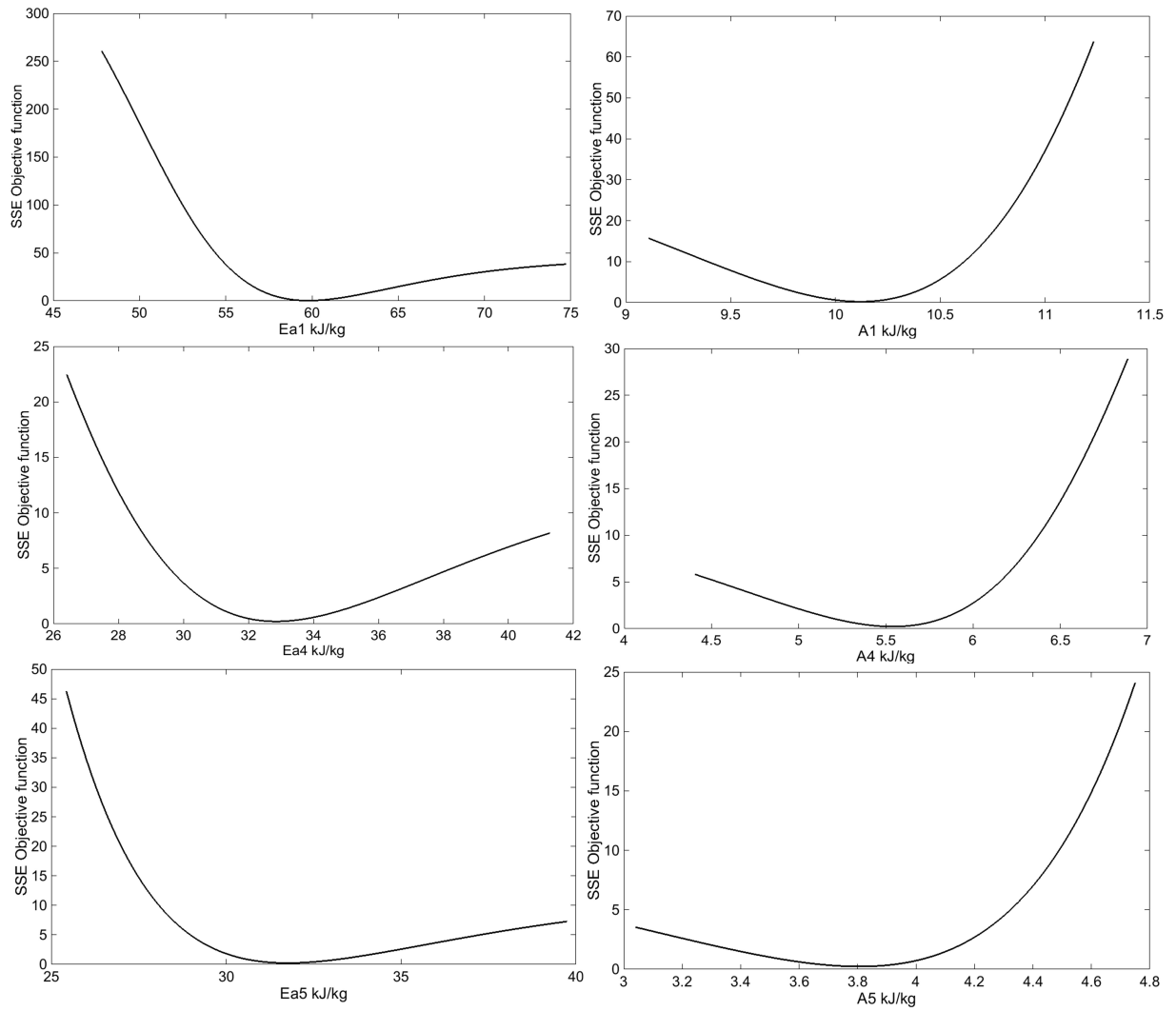
When applied to HC, FCC and DC for databases with 99, 84 and 36 data points respectively, the coefficient of determination ( $R^2$ ) between model predictions with the global kinetic model and experiments were 0.96 (HC), 0.69 (FCC) and 0.84 (DC). Despite the differences in  $R^2$ , all the kinetic models calculated give a good representation of experimental data that was not included in the original XML database.

Some future work that would improve the results here obtained: a) increase the size and quality of the XML database by a constant review of the open literature and the consideration

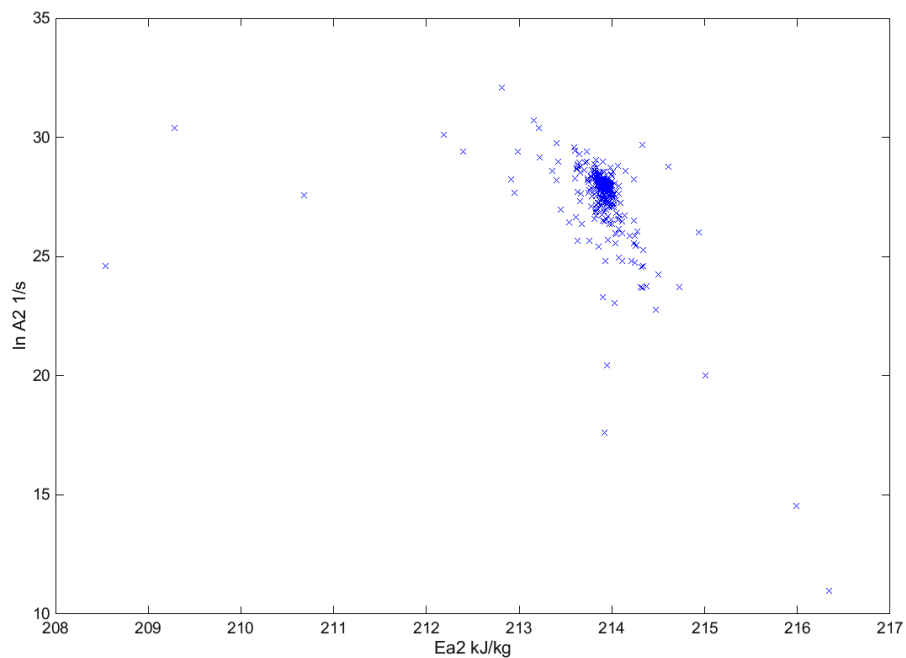
of other important parameters to the tree-structure such as goodness of the mass balance closure of the experiments and the evaluation of the extent of mass transfer limitations and catalyst deactivation in the experiment; b) a more complete uncertainty analysis should be carried out assuming uncertainties for the experimental data and c) A more effective and robust uncertainty analysis using a bayesian parameter estimation.

## A. Main statistical properties for Hydrocracking

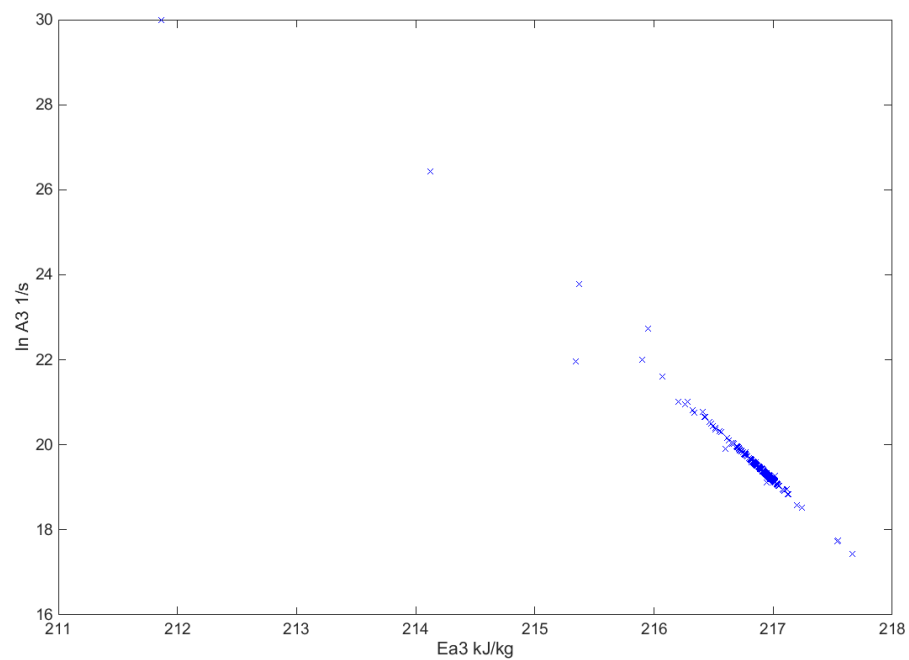
Figure **A-1** shows the sensitivity analysis carried out for some of reactions for HC process. All of them show the local minimum in the optimized value. Figure **A-2** to Figure **A-6** show the dispersion and the compensation effect for each of couple of kinetic parameters for HC reaction system. After, a series of histograms show the distribution function for each kinetic parameter as we can see in Figure **A-7** to Figure **A-11**.



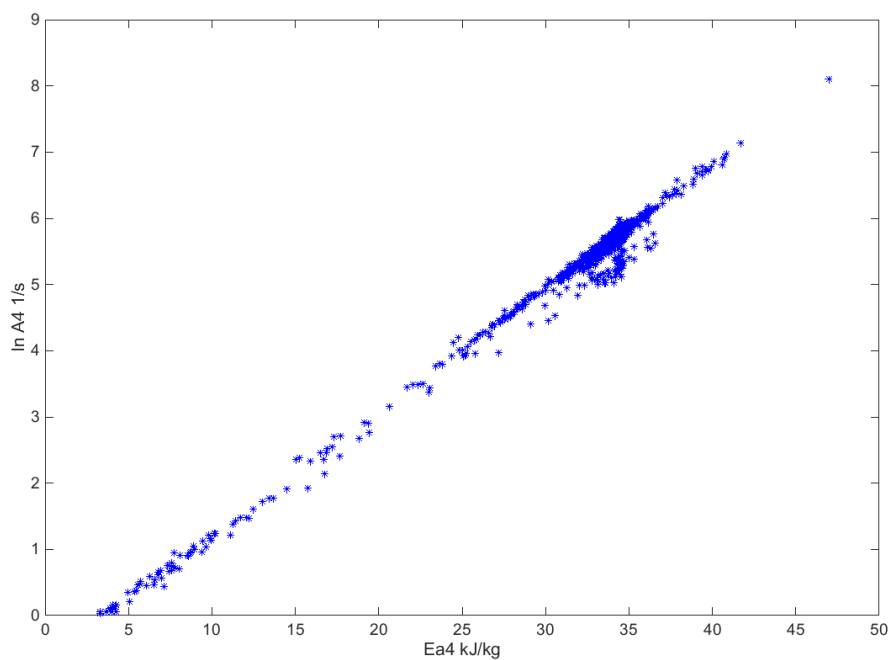
**Figure A-1.** Sensitivity for activation energy and preexponential factor of the main reactions in HC



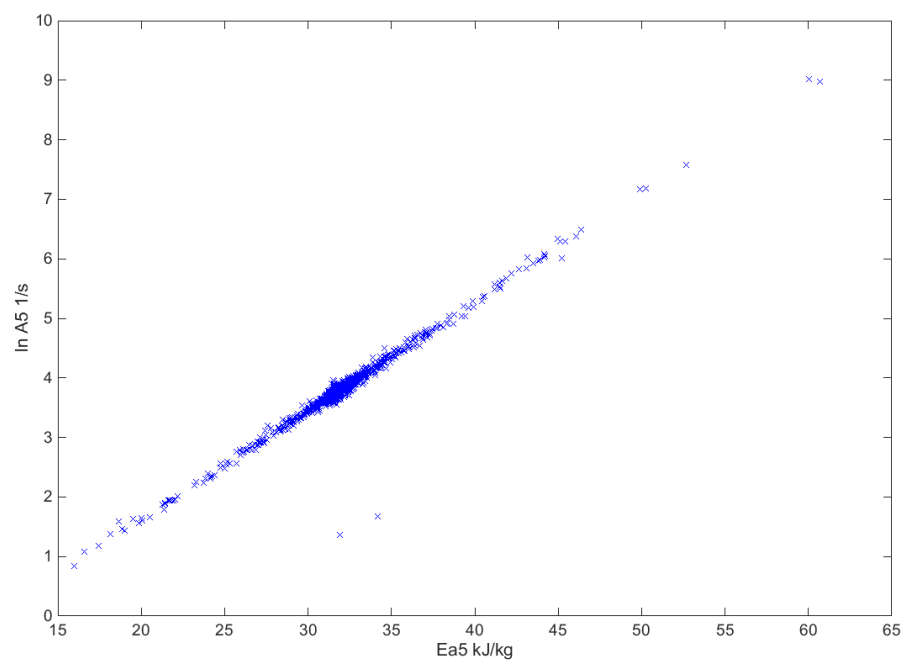
**Figure A-2.** Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 2



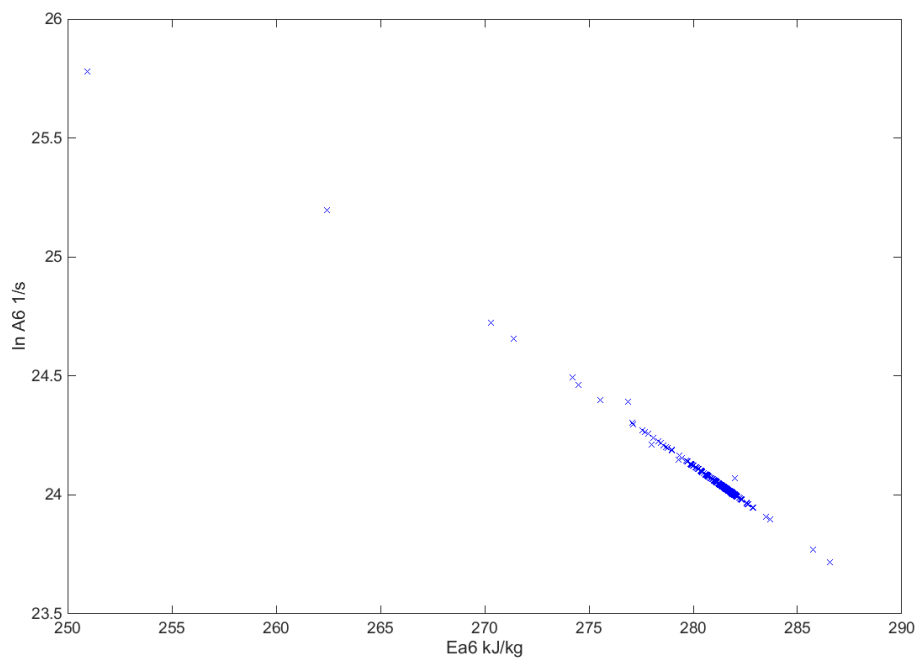
**Figure A-3.** Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 3



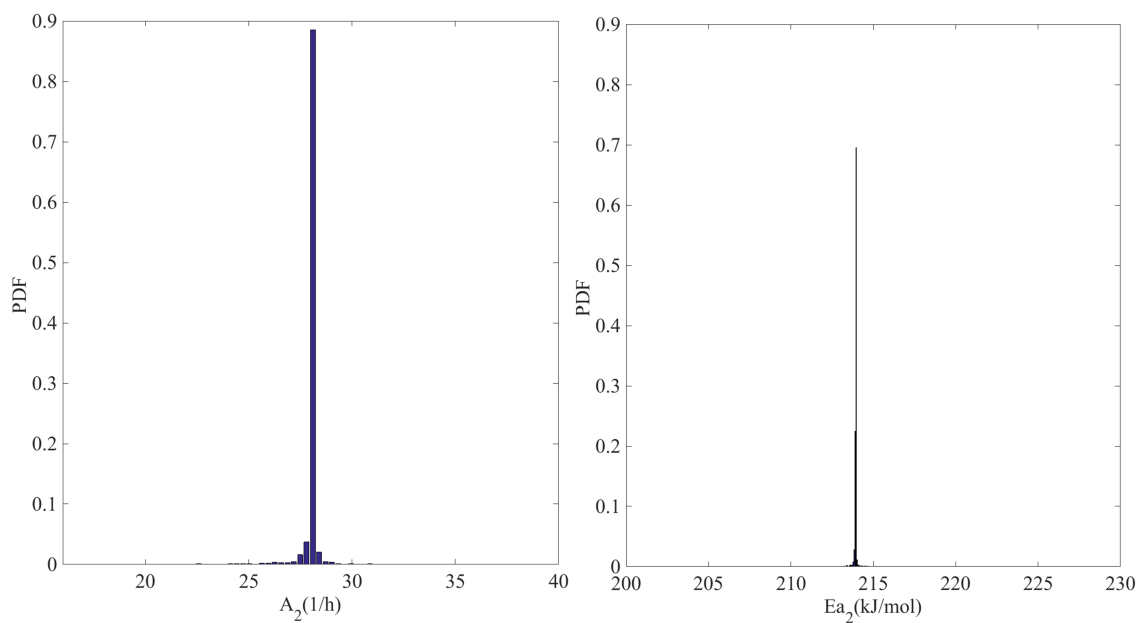
**Figure A-4.** Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 4



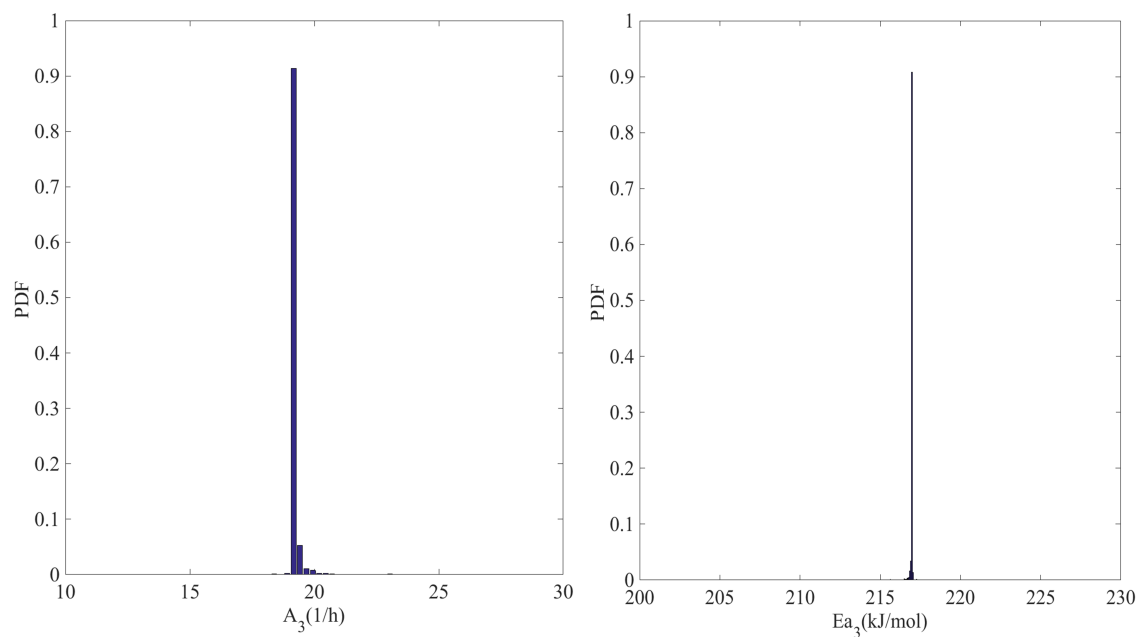
**Figure A-5.** Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 5



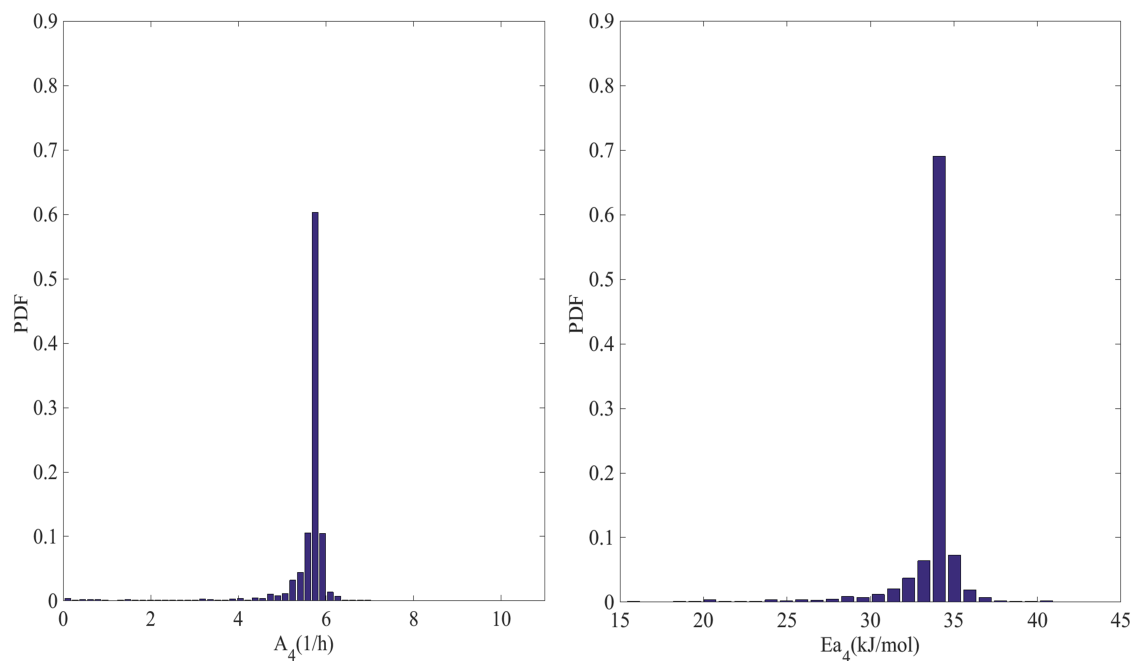
**Figure A-6.** Dispersion points that show the distribution of the couple of the kinetic parameters corresponding to reaction 6



**Figure A-7.** histograms for the distribution of values for the kinetic parameters corresponding to reaction 2

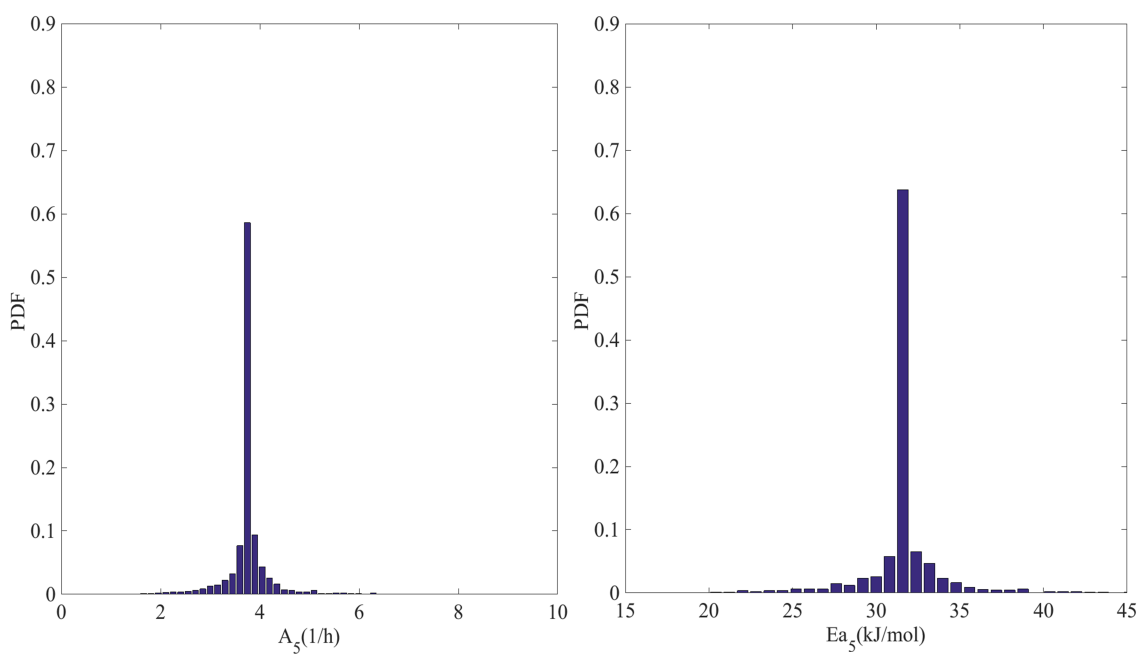


**Figure A-8.** histograms for the distribution of values for the kinetic parameters corresponding to reaction 3

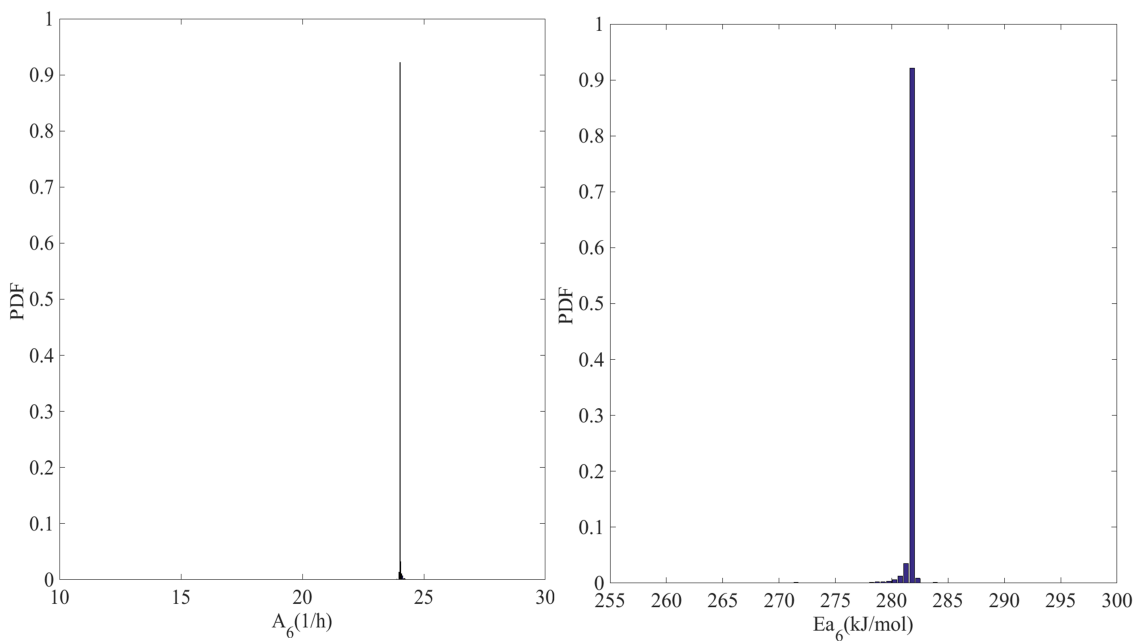


**Figure A-9.** histograms for the distribution of values for the kinetic parameters corresponding to reaction 4





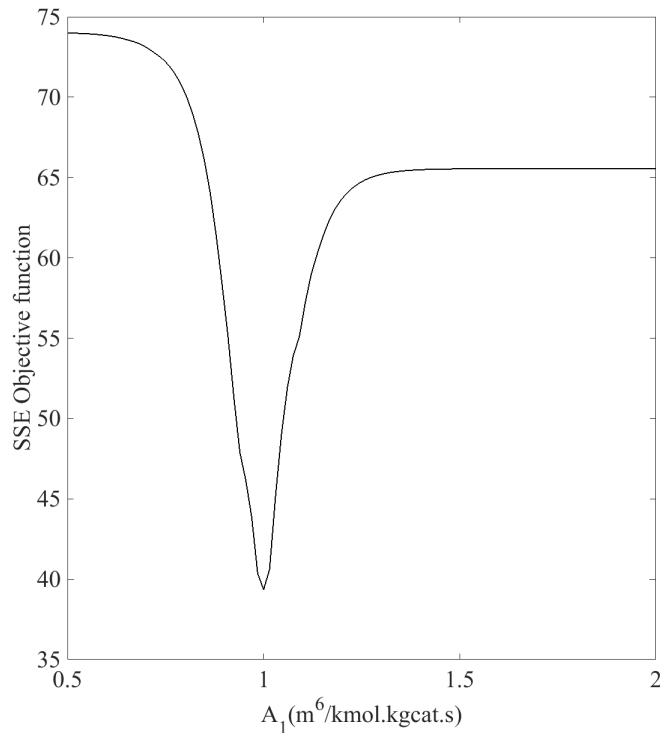
**Figure A-10.** histograms for the distribution of values for the kinetic parameters corresponding to reaction 5



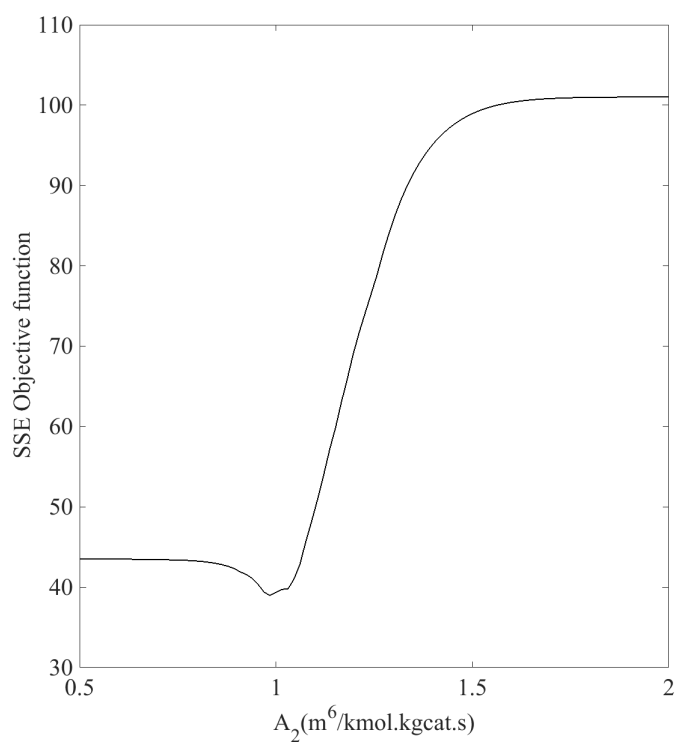
**Figure A-11.** histograms for the distribution of values for the kinetic parameters corresponding to reaction 6

## B. Main statistical properties for Fluid Catalytic Cracking

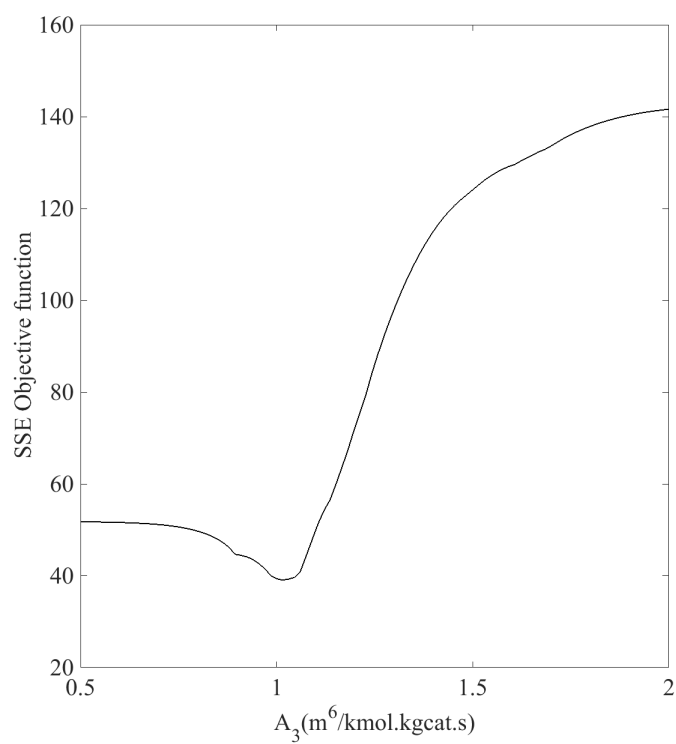
Similarly than HC process this Appendix show the main properties for FCC. Figure **B-1** to Figure **B-4** shows the sensitivity analysis carried out for some of reactions for FCC process. All of them show the local minimum in the optimized value. Figure **B-5** to Figure **B-8** show the dispersion and the histograms as a distribution function for each set of kinetic parameter.



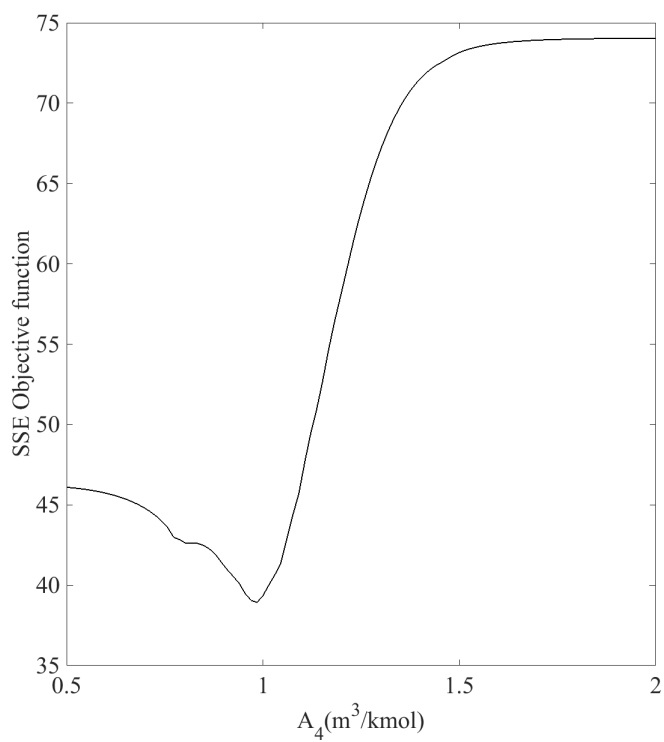
**Figure B-1.** Sensitivity for the pre-exponential factor of reaction 1



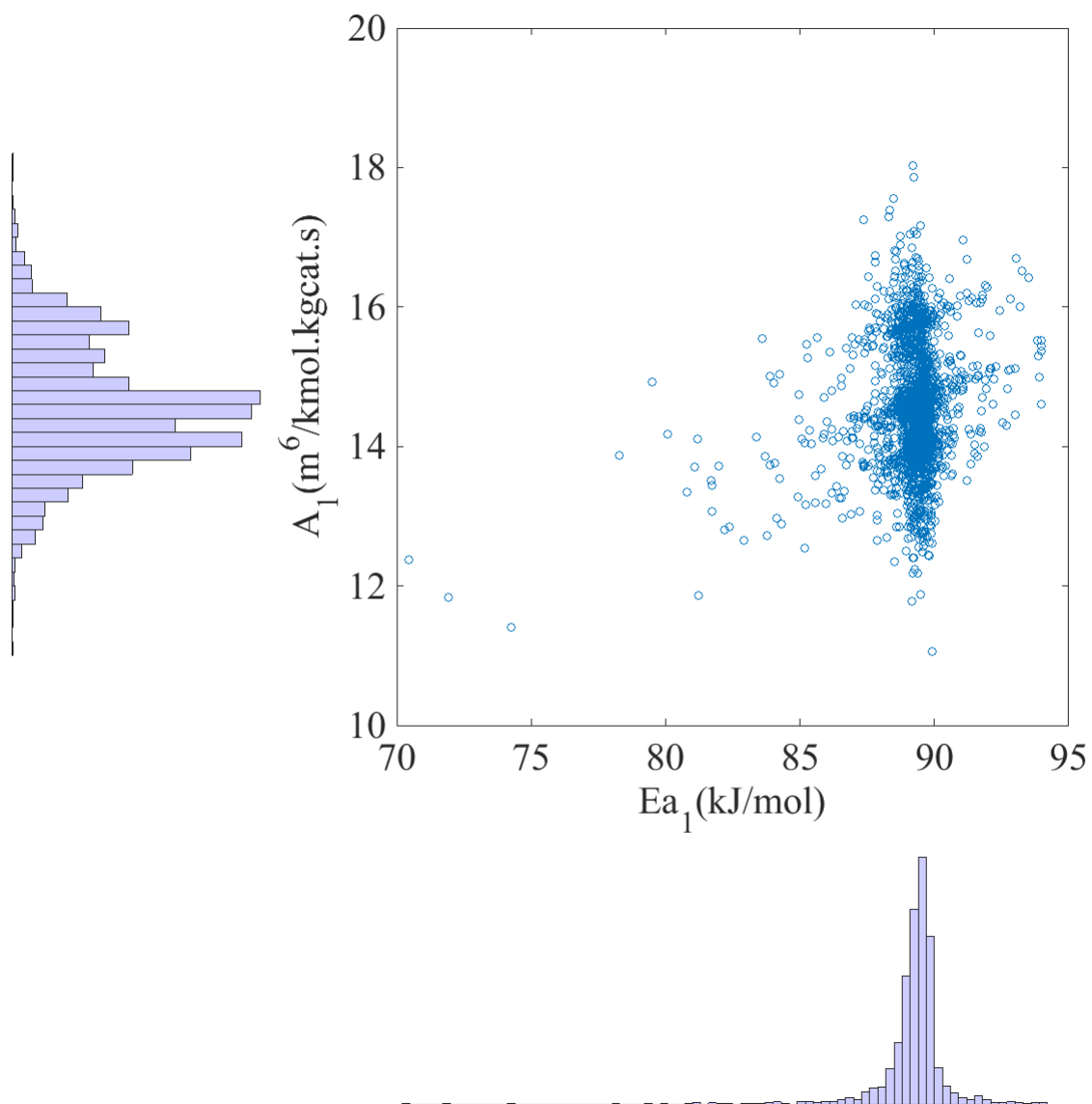
**Figure B-2.** Sensitivity for the pre-exponential factor of reaction 1



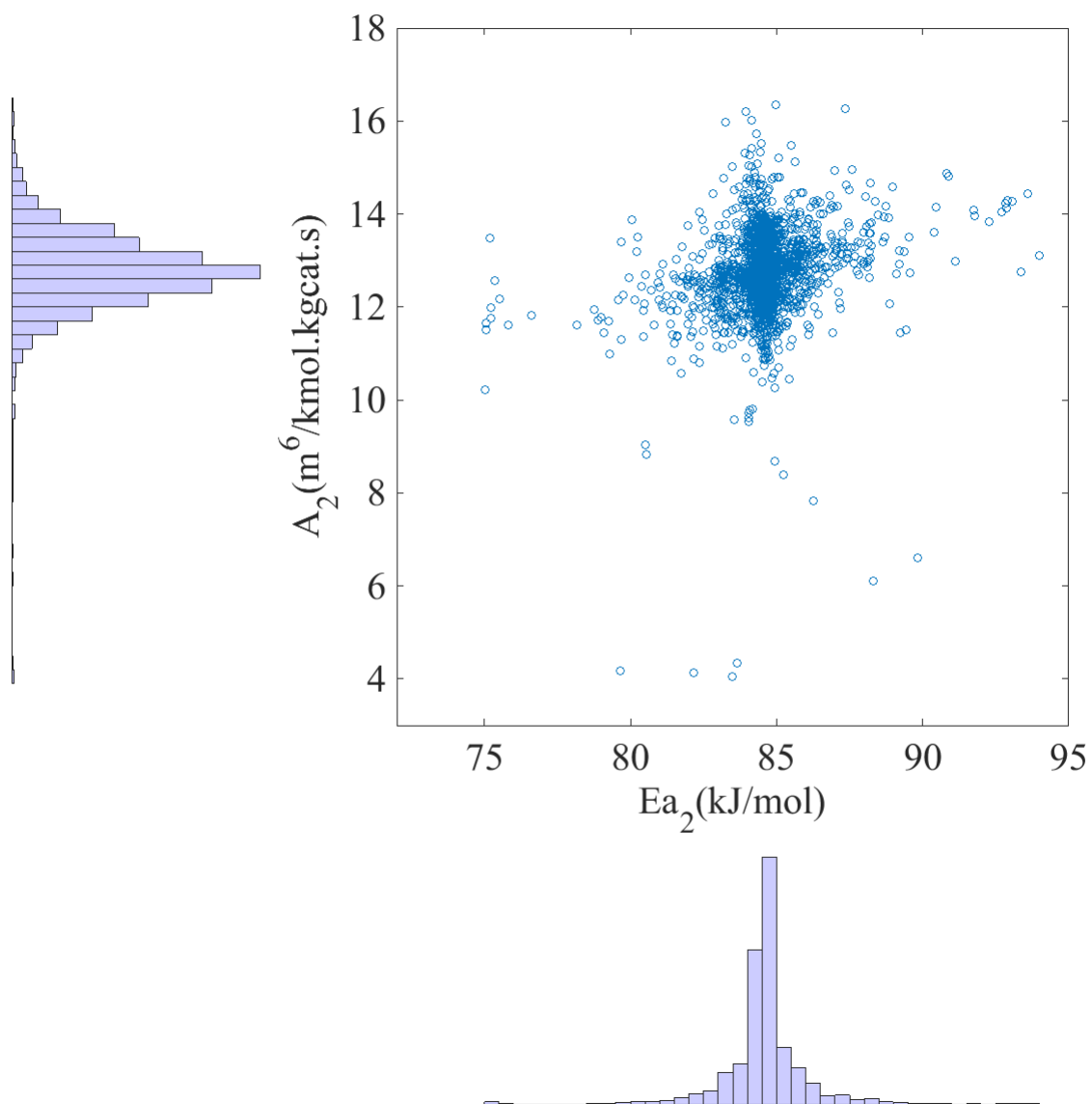
**Figure B-3.** Sensitivity for the pre-exponential factor of reaction 1



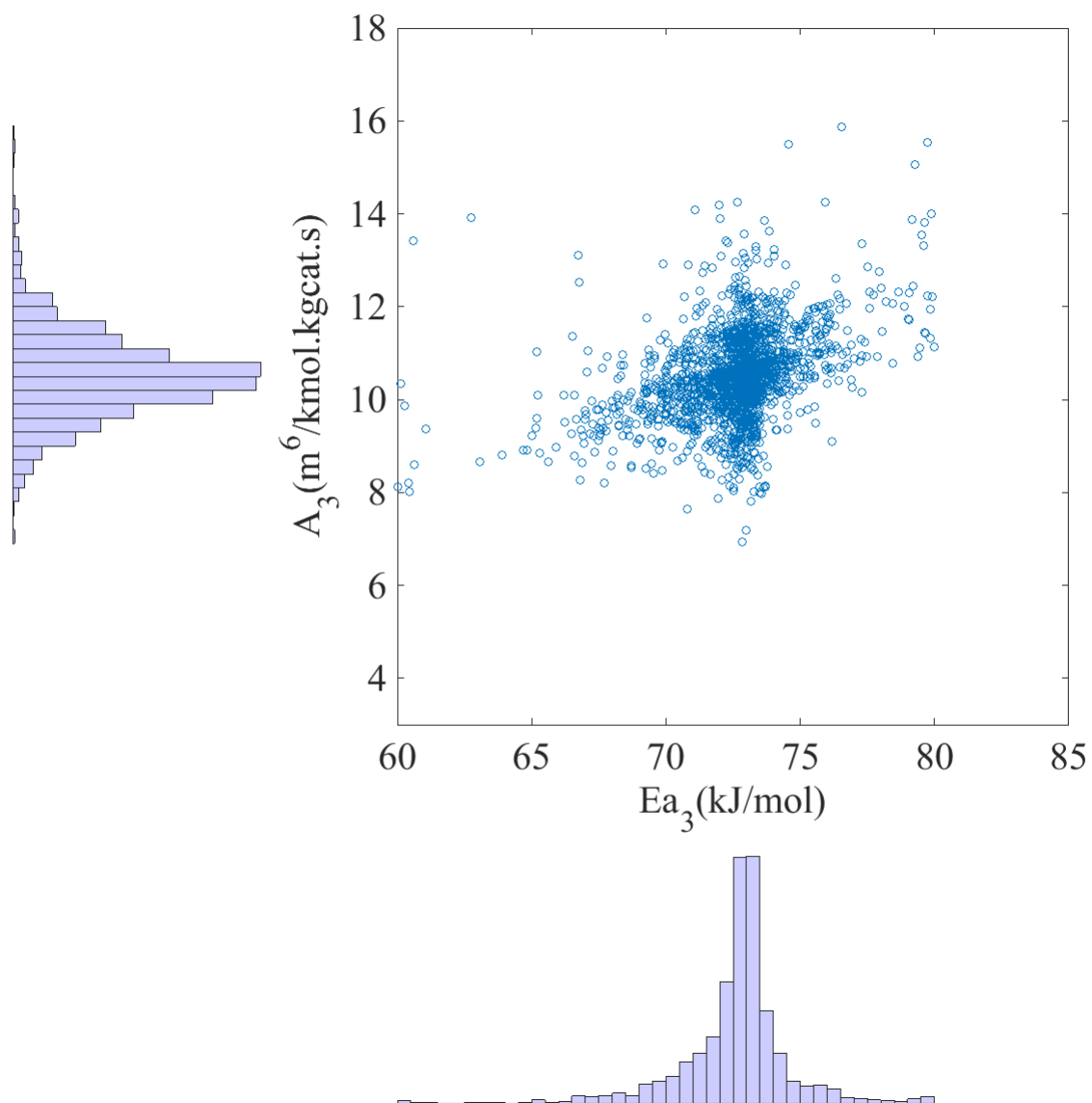
**Figure B-4.** Sensitivity for the pre-exponential factor of reaction 1



**Figure B-5.** distribution of kinetic parameters for reaction 1

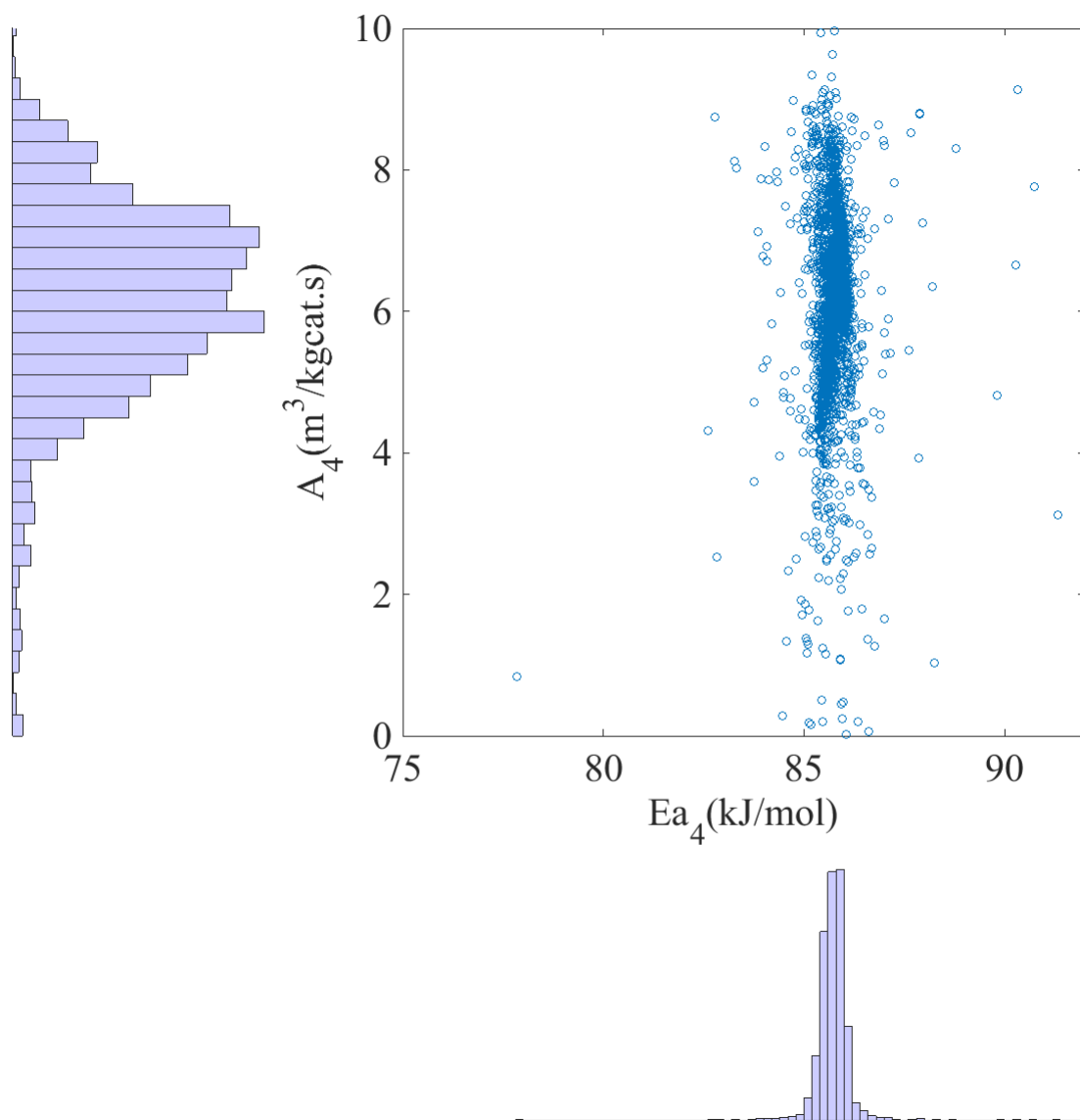


**Figure B-6.** distribution of kinetic parameters for reaction 2



**Figure B-7.** distribution of kinetic parameters for reaction 3

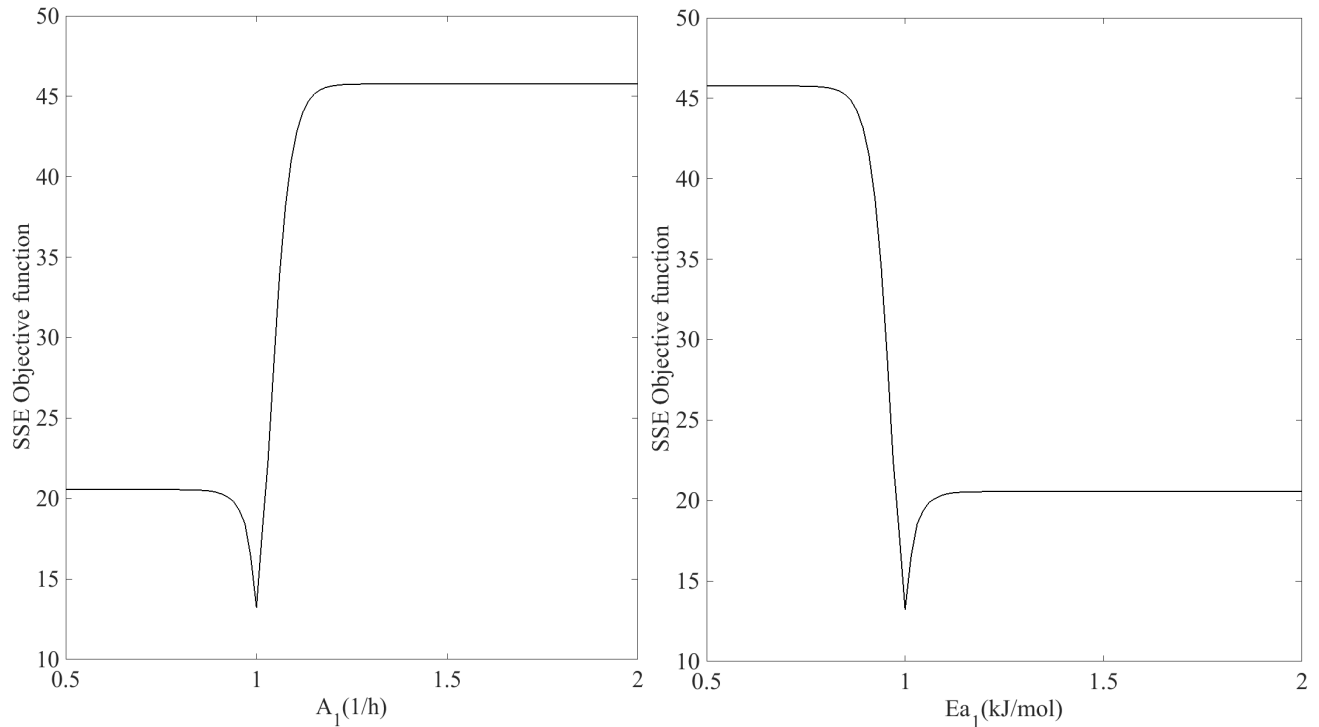




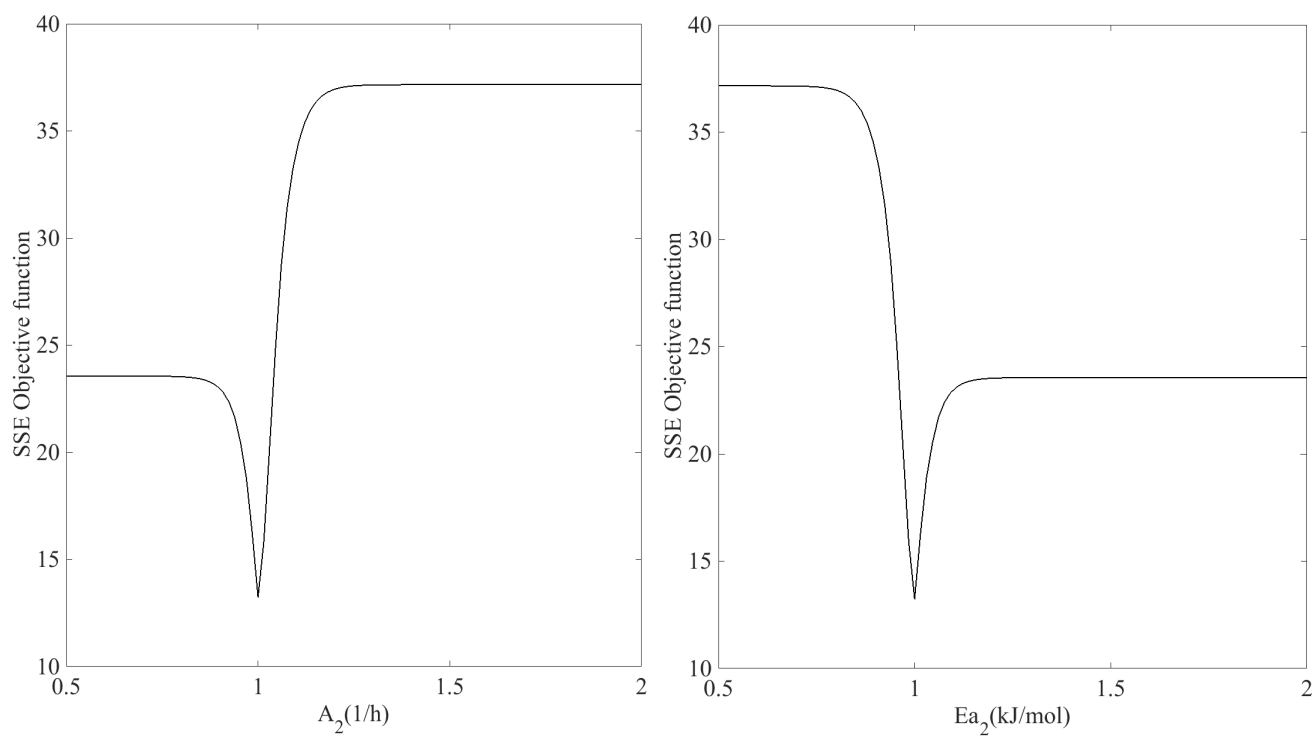
**Figure B-8.** distribution of kinetic parameters for reaction 4

## C. Main statistical properties for Delayed Coking

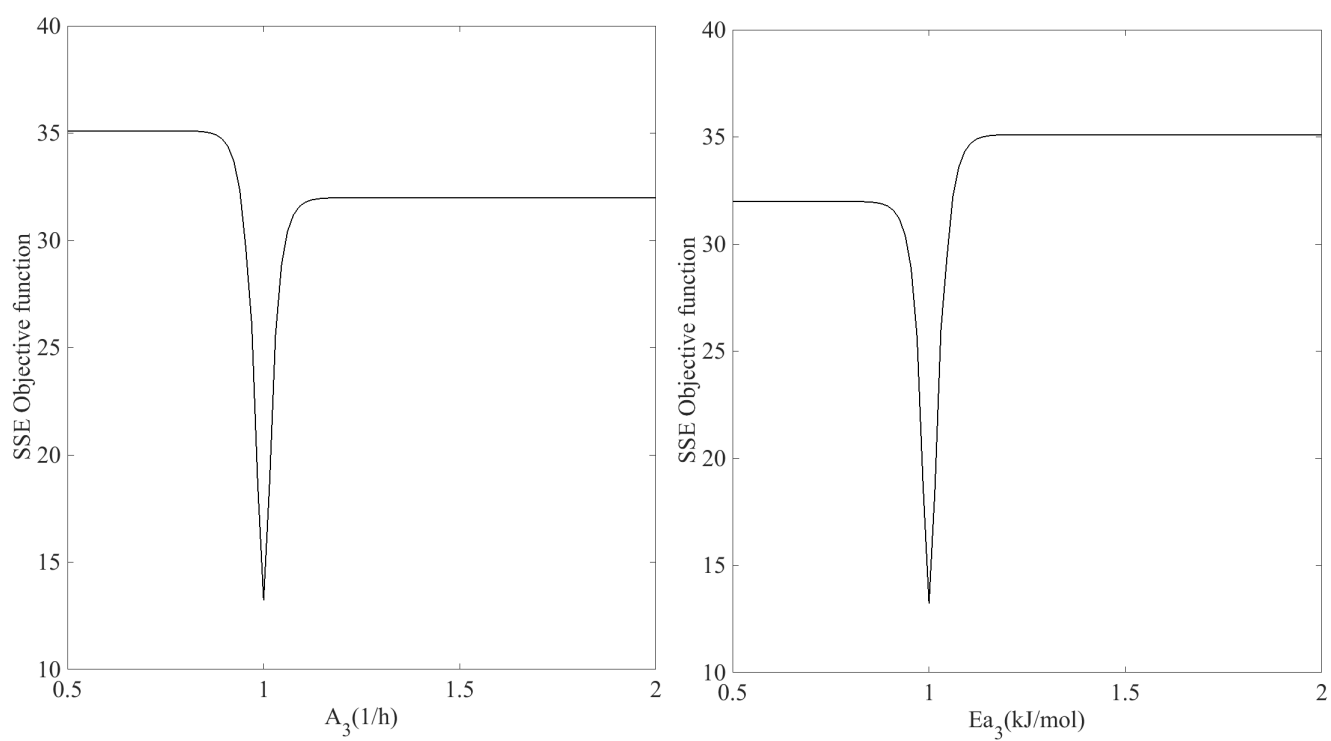
This Appendix show the main properties for DC. Figure C-1 to Figure C-3 shows the sensitivity analysis carried out for some of reactions for FCC process. All of them show the local minimum in the optimized value. Figure C-4 to Figure C-6 show the dispersion and the histograms as a distribution function for each set of kinetic parameter.



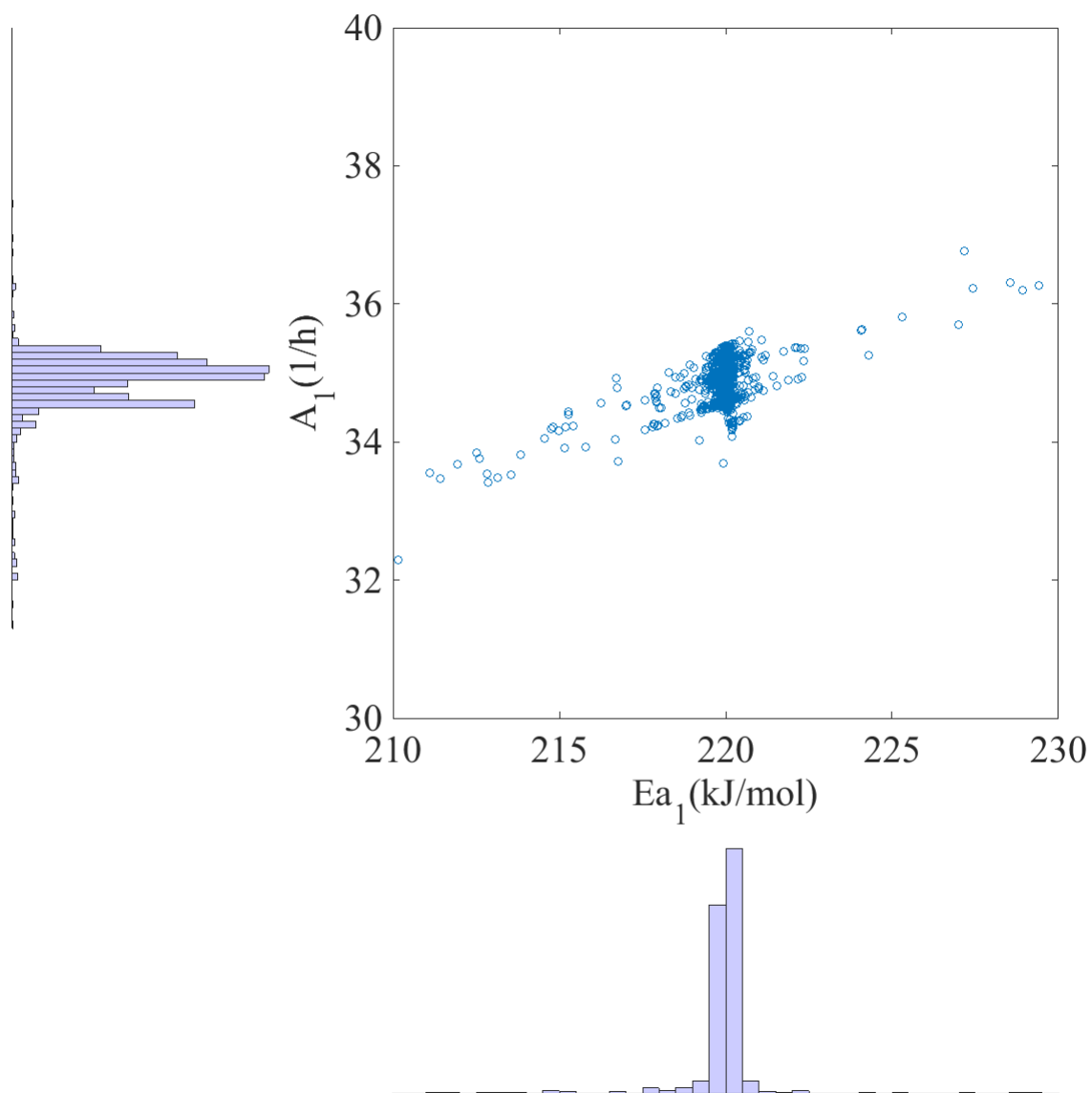
**Figure C-1.** Sensitivity analysis for kinetic parameters corresponding to reaction 1



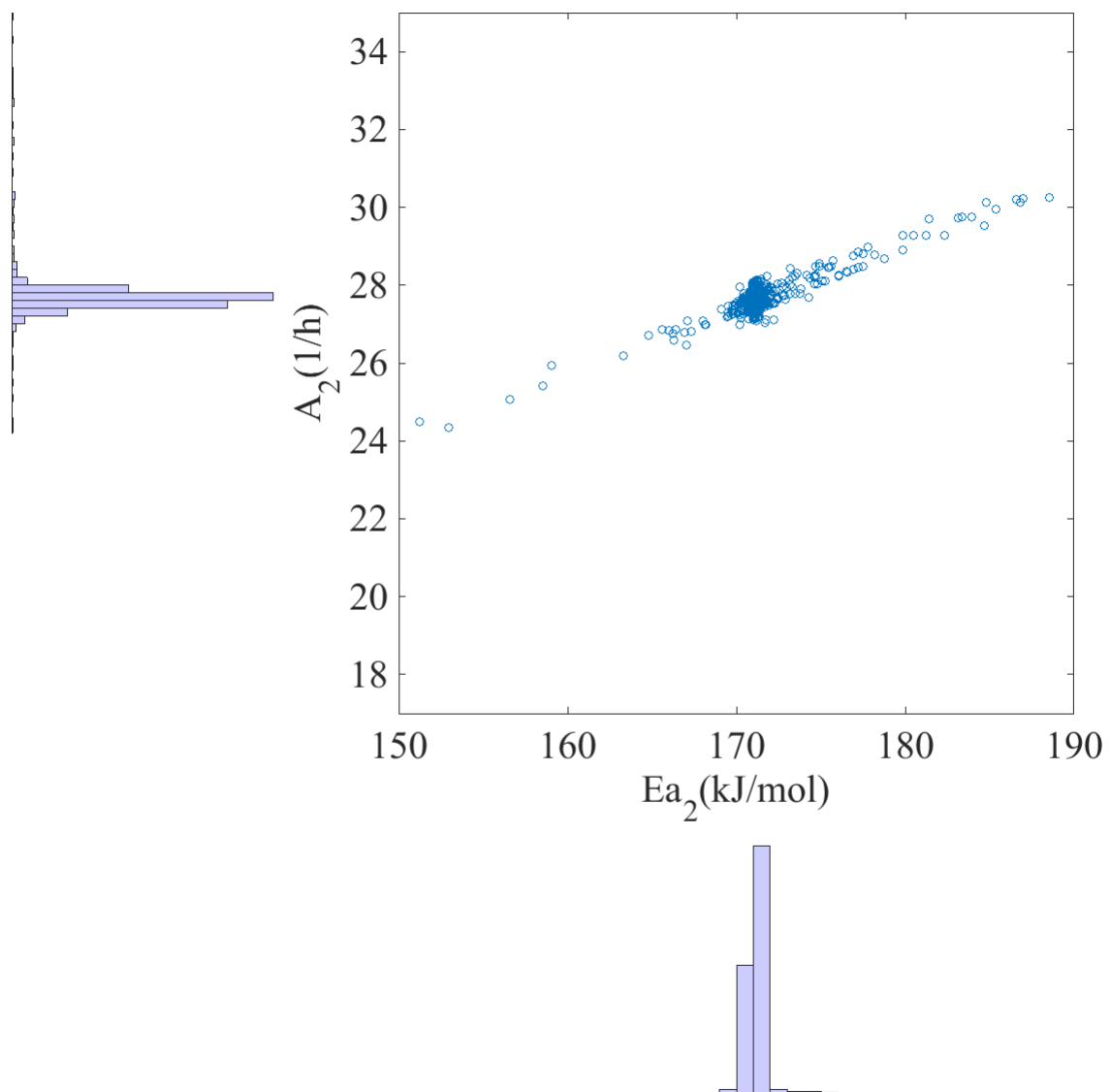
**Figure C-2.** Sensitivity analysis for kinetic parameters corresponding to reaction 2



**Figure C-3.** Sensitivity analysis for kinetic parameters corresponding to reaction3



**Figure C-4.** distribution of kinetic parameters for reaction 1



**Figure C-5.** distribution of kinetic parameters for reaction 2

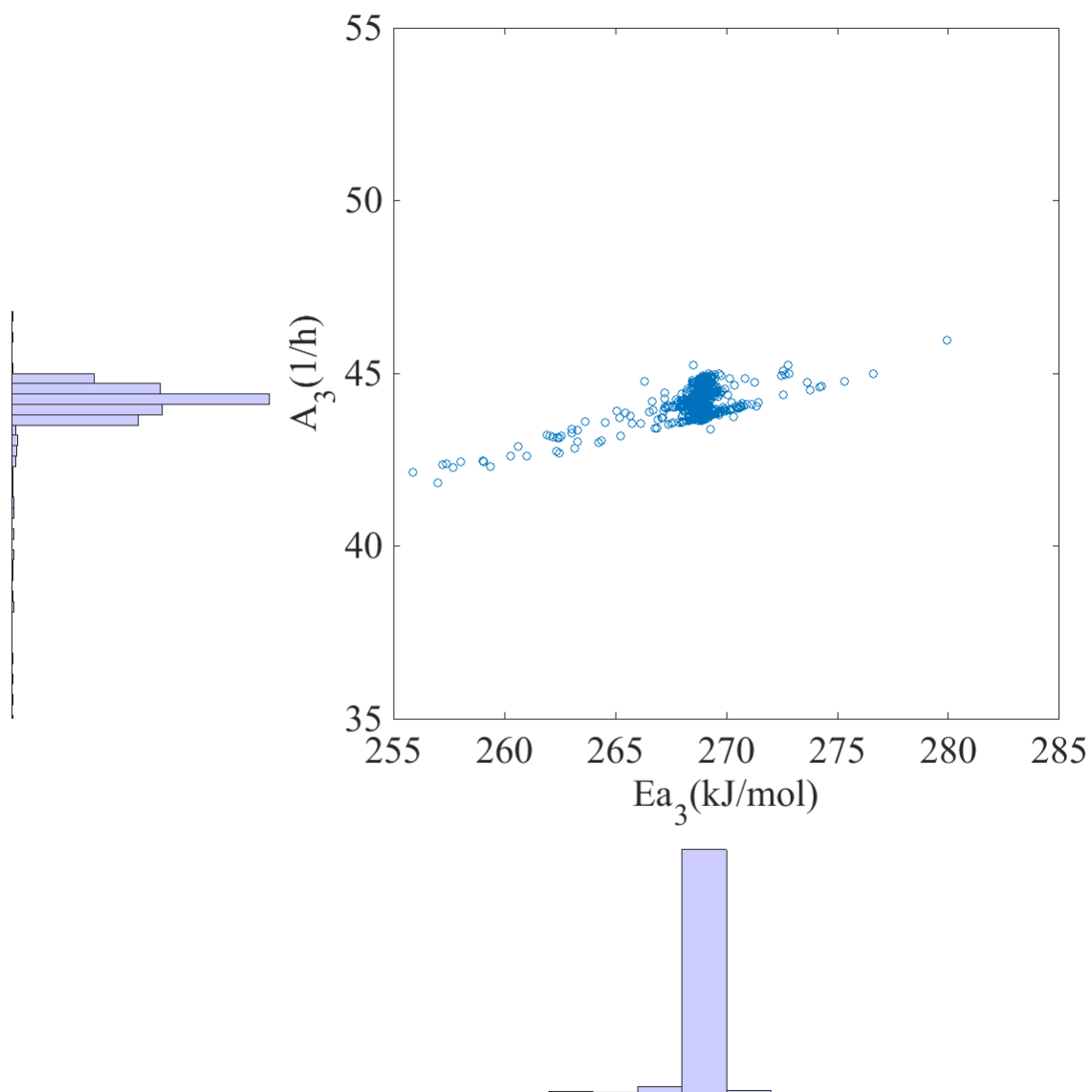
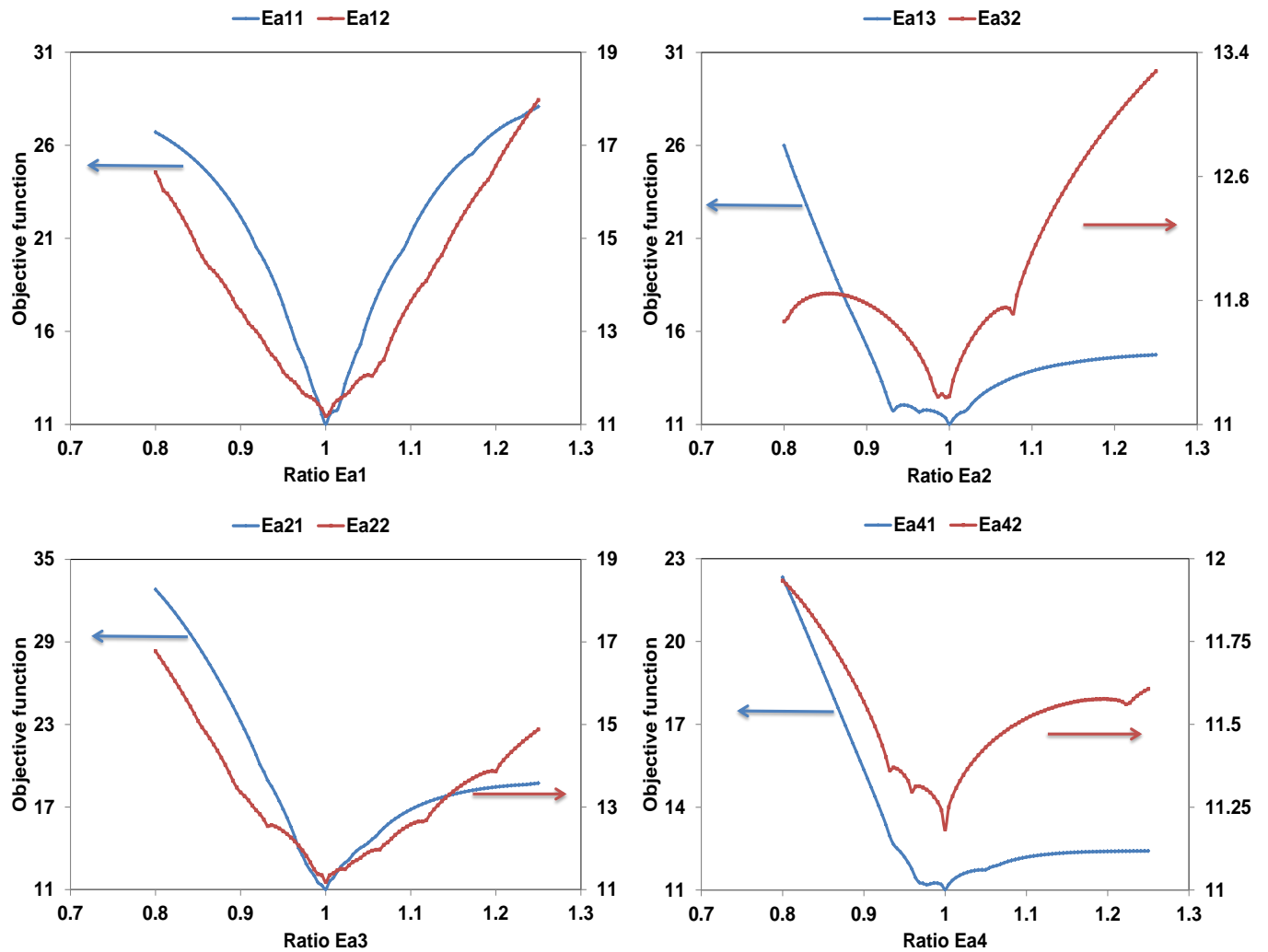


Figure C-6. distribution of kinetic parameters for reaction 3

**D. Differences between the type of Arrhenius equation in the Sensitivity Analysis**





**Figure D-1.** value of the objective function when use both Arrhenius equation. Red line: Eq. number 1. Blue line: Eq. number 2

## **E. XML data base for HC, FCC and DC**

```

<?xml version="1.0" encoding="utf-8"?>
<Mechanisms>
  <FCC>
    <Mechanism1>
      <Name>Jacob</Name>
      <Lumps>10</Lumps>
      <Year>1976</Year>
      <speciesData id="species_data">
        <species1 name="Ph">
          <density units="kg/m3">900</density>
          <PesoM units="kg/kmol">400</PesoM>
        </species1>
        <species2 name="Nh">
          <density units="kg/m3">850</density>
          <PesoM units="kg/kmol">400</PesoM>
        </species2>
        <species3 name="Ah">
          <density units="kg/m3">875</density>
          <PesoM units="kg/kmol">400</PesoM>
        </species3>
        <species4 name="Cah">
          <density units="kg/m3">880</density>
          <PesoM units="kg/kmol">400</PesoM>
        </species4>
        <species5 name="P1">
          <density units="kg/m3">750</density>
          <PesoM units="kg/kmol">200</PesoM>
        </species5>
        <species6 name="N1">
          <density units="kg/m3">775</density>
          <PesoM units="kg/kmol">200</PesoM>
        </species6>
        <species7 name="A1">
          <density units="kg/m3">780</density>
          <PesoM units="kg/kmol">200</PesoM>
        </species7>
        <species8 name="Cal">
          <density units="kg/m3">715</density>
          <PesoM units="kg/kmol">200</PesoM>
        </species8>
        <species9 name="Gas">
          <density units="kg/m3">100</density>
          <PesoM units="kg/kmol">50</PesoM>
        </species9>
        <species10 name="coque">
          <density units="kg/m3">1800</density>
          <PesoM units="kg/kmol">12</PesoM>
        </species10>
      </speciesData>
      <reactionData id="reaction_data">
        <reaction id="01" Reversible="No">
          <Equation>Ph--&gt;P1</Equation>
          <Ratecoeff>
            <ActEner units="Btu/lbmol">26100</ActEner>
            <Rate units="1/s">0.196<!--at 1000°F--></Rate>
            <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
          </Ratecoeff>
          <Reactants>Ph</Reactants>
          <Products>P1</Products>
        </reaction>
        <reaction id="02" Reversible="No">
          <Equation>Nh--&gt;N1</Equation>
          <Ratecoeff>
            <ActEner units="Btu/lbmol">26100</ActEner>
            <Rate units="1/s">0.196<!--at 1000°F--></Rate>
            <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
          </Ratecoeff>
          <Reactants>Nh</Reactants>
          <Products>N1</Products>
        </reaction>
        <reaction id="03" Reversible="No">

```

```

<Equation>Ah--&gt;Al</Equation>
<Ratecoeff>
  <ActEner units="Btu/lbmol">26100</ActEner>
  <Rate units="1/s">0.196<!--at 1000°F--></Rate>
  <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>Ah</Reactants>
<Products>Al</Products>
</reaction>
<reaction id="04" Reversible="No">
  <Equation>Ah--&gt;Rl</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.489<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>Rl</Products>
</reaction>
<reaction id="05" Reversible="No">
  <Equation>Rh--&gt;Rl</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.049<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Rh</Reactants>
  <Products>Rl</Products>
</reaction>
<reaction id="06" Reversible="No">
  <Equation>Ph--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.611<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="07" Reversible="No">
  <Equation>Nh--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.939<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="08" Reversible="No">
  <Equation>Ah--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.685<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="09" Reversible="No">
  <Equation>Ph--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.099<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="10" Reversible="No">
  <Equation>Nh--&gt;Coque</Equation>

```

```

<Ratecoeff>
  <ActEner units="Btu/lbmol">31500</ActEner>
  <Rate units="1/s">0.149<!--at 1000°F--></Rate>
  <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>Nh</Reactants>
<Products>Coque</Products>
</reaction>
<reaction id="11" Reversible="No">
  <Equation>Ah--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.198<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="12" Reversible="No">
  <Equation>Rh--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.149<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Rh</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="13" Reversible="No">
  <Equation>P1--&gt;g</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.282<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>P1</Reactants>
  <Products>g</Products>
</reaction>
<reaction id="14" Reversible="No">
  <Equation>N1--&gt;g</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.282<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>N1</Reactants>
  <Products>g</Products>
</reaction>
<reaction id="15" Reversible="No">
  <Equation>A1--&gt;g</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.196<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>A1</Reactants>
  <Products>g</Products>
</reaction>
<reaction id="16" Reversible="No">
  <Equation>P1--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.099<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>P1</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="17" Reversible="No">
  <Equation>N1--&gt;coque</Equation>
  <Ratecoeff>

```

```

    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.099<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>N1</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="18" Reversible="No">
  <Equation>A1--&gt;c</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.050<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>A1</Reactants>
  <Products>c</Products>
</reaction>
<reaction id="19" Reversible="No">
  <Equation>R1--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.01<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>R1</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="20" Reversible="No">
  <Equation>g--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">18000</ActEner>
    <Rate units="1/s">0.048<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>g</Reactants>
  <Products>coque</Products>
</reaction>
</reactionData>
</Mechanism1>
<Mechanism2>
  <Name>Weekman</Name>
  <Lumps>3</Lumps>
  <Year>1970</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species2>
    <species3 name="Gas+coke">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species3>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>GO--&gt;Gasoline</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.1942</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gasoline</Products>
    </reaction>
    <reaction id="2" Reversible="No">
      <Equation>Gasoline--&gt;Gas+coke</Equation>
      <Ratecoeff>
        <velcons units="s^-1">0.0093</velcons>
      </Ratecoeff>

```

```

    <Reactants>Gasoline</Reactants>
    <Products>Gas+coke</Products>
  </reaction>
  <reaction id="3" Reversible="No">
    <Equation>GO--&gt;gas+coke</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0488</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>gas+coke</Products>
  </reaction>
</reactionData>
</Mechanism2>
<Mechanism3>
  <Name>Lee</Name>
  <Lumps>4</Lumps>
  <Year>1989</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>GO--&gt;Gasoline</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.1942</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gasoline</Products>
    </reaction>
    <reaction id="2" Reversible="No">
      <Equation>GO--&gt;Gas</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.0348</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gas</Products>
    </reaction>
    <reaction id="3" Reversible="No">
      <Equation>GO--&gt;coke</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.0140</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>coke</Products>
    </reaction>
    <reaction id="4" Reversible="No">
      <Equation>Gne--&gt;Gas</Equation>
      <Ratecoeff>
        <velcons units=" s^-1">0.0093</velcons>
      </Ratecoeff>
      <Reactants>Gne</Reactants>
      <Products>Gas</Products>
    </reaction>
    <reaction id="5" Reversible="No">
      <Equation>Gne--Coke</Equation>
      <Ratecoeff>

```

```

    <velcons units="s^-1">0.0000002</velcons>
  </Ratecoeff>
  <Reactants>Gne</Reactants>
  <Products>Coke</Products>
</reaction>
</reactionData>
</Mechanism3>
<Mechanism4>
  <Name>Iarocca</Name>
  <Lumps>5</Lumps>
  <Year>1990</Year>
  <speciesData id="species_data">
    <species1 name="SVG0">
      <sgravity units="-o-">0.9389</sgravity>
      <TBP units="K">
        <IBP>534</IBP>
        <wt5>573</wt5>
        <wt10>595</wt10>
        <wt30>630</wt30>
        <wt50>660</wt50>
        <wt70>696</wt70>
        <wt90>747</wt90>
        <wt95>771</wt95>
        <FBP>817</FBP>
      </TBP>
    </species1>
    <species2 name="ParafinivGO">
      <sgravity units="-o-">0.9039</sgravity>
      <TBP units="K">
        <IBP>482</IBP>
        <wt5>537</wt5>
        <wt10>558</wt10>
        <wt30>609</wt30>
        <wt50>648</wt50>
        <wt70>691</wt70>
        <wt90>743</wt90>
        <wt95>765</wt95>
        <FBP>817</FBP>
      </TBP>
    </species2>
    <species3 name="P">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="N">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
    <species5 name="A">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species5>
    <species6 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species6>
    <species7 name="gas+coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species7>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>P--&gt;gas+coke</Equation>
      <Ratecoeff>
        <velcons units="cm^3 gcat^-1 s^-1">6.6</velcons>
      </Ratecoeff>
      <Reactants>P</Reactants>
      <Products>gas+coke</Products>
    </reaction>
    <reaction id="2" Reversible="No">

```



```

    <Equation>P--&gt;Gne</Equation>
    <Ratecoeff>
      <velcons units="cm^3 gcat^-1 s^-1">6.6</velcons>
    </Ratecoeff>
    <Reactants>P</Reactants>
    <Products>Gne</Products>
  </reaction>
  <reaction id="3" Reversible="No">
    <Equation>N--&gt;gas+coke</Equation>
    <Ratecoeff>
      <velcons units="cm^3 gcat^-1 s^-1">1.4</velcons>
    </Ratecoeff>
    <Reactants>N</Reactants>
    <Products>gas+coke</Products>
  </reaction>
  <reaction id="4" Reversible="No">
    <Equation>N--&gt;Gne</Equation>
    <Ratecoeff>
      <velcons units="cm^3 gcat^-1 s^-1">7.1</velcons>
    </Ratecoeff>
    <Reactants>N</Reactants>
    <Products>Gne</Products>
  </reaction>
  <reaction id="5" Reversible="No">
    <Equation>A--&gt;gas+coke</Equation>
    <Ratecoeff>
      <velcons units="cm^3 gcat^-1 s^-1">1.1</velcons>
    </Ratecoeff>
    <Reactants>A</Reactants>
    <Products>gas+coke</Products>
  </reaction>
  <reaction id="6" Reversible="No">
    <Equation>A--&gt;Gne</Equation>
    <Ratecoeff>
      <velcons units="cm^3 gcat^-1 s^-1">17.1</velcons>
    </Ratecoeff>
    <Reactants>A</Reactants>
    <Products>Gne</Products>
  </reaction>
</reactionData>
</Mechanism4>
<Mechanism5>
  <Name>Ancheyta</Name>
  <Lumps>5</Lumps>
  <Year>1997</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <API units="">25.5</API>
      <TBP units="k">
        <IBP>508</IBP>
        <wt30>682</wt30>
        <wt50>706</wt50>
        <wt70>740</wt70>
        <wt90>790</wt90>
        <FBP>841</FBP>
      </TBP>
      <sgravity units="-o-">0.9013</sgravity>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Dry Gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
    <species5 name="LPG">

```

```

    <density units="kg/m3">-0-</density>
    <PesoM units="kg/kmol">-0-</PesoM>
  </species5>
</speciesData>
<reactionData id="reaction_data">
  <reaction id="1" Reversible="No">
    <Equation>GO--&gt;Gasoline</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.1942</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>Gasoline</Products>
  </reaction>
  <reaction id="2" Reversible="No">
    <Equation>GO--&gt;LPG</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0357</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>LPG</Products>
  </reaction>
  <reaction id="3" Reversible="No">
    <Equation>GO--&gt;DG</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0001</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>DG</Products>
  </reaction>
  <reaction id="4" Reversible="No">
    <Equation>GO--&gt;coke</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0140</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>coke</Products>
  </reaction>
  <reaction id="5" Reversible="No">
    <Equation>Gne--&gt;LPG</Equation>
    <Ratecoeff>
      <velcons units="s^-1">0.0061</velcons>
    </Ratecoeff>
    <Reactants>Gne</Reactants>
    <Products>LPG</Products>
  </reaction>
  <reaction id="6" Reversible="No">
    <Equation>Gne--&gt;DG</Equation>
    <Ratecoeff>
      <velcons units=" s^-1">0.0032</velcons>
    </Ratecoeff>
    <Reactants>Gne</Reactants>
    <Products>DG</Products>
  </reaction>
  <reaction id="7" Reversible="No">
    <Equation>Gne--&gt;coke</Equation>
    <Ratecoeff>
      <velcons units=" s^-1">0.0000002</velcons>
    </Ratecoeff>
    <Reactants>Gne</Reactants>
    <Products>coke</Products>
  </reaction>
  <reaction id="8" Reversible="No">
    <Equation>LPG--&gt;DG</Equation>
    <Ratecoeff>
      <velcons units=" s^-1">0.0020</velcons>
    </Ratecoeff>
    <Reactants>LPG</Reactants>
    <Products>DG</Products>
  </reaction>
</reactionData>
</Mechanism5>

```

```

<Mechanism6>
  <Name>Hagelberg</Name>
  <Lumps>8</Lumps>
  <Year>2002</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="Gparafins">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Golefins">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="Gnaphthenes">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
    <species5 name="Garomatics">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species5>
    <species6 name="LPG">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species6>
    <species name="Dry Gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species>
    <species8 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species8>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>GO--&gt;Gparafins</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.024</velcons>
        <ActEner units="kJ/mol">75</ActEner>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gparafins</Products>
    </reaction>
    <reaction id="2" Reversible="No">
      <Equation>GO--&gt;Golefins</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.044</velcons>
        <ActEner units="kJ/mol">106</ActEner>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Golefins</Products>
    </reaction>
    <reaction id="3" Reversible="No">
      <Equation>GO--&gt;Gnaphthenes</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.009</velcons>
        <ActEner units="kJ/mol">68</ActEner>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gnaphthenes</Products>
    </reaction>
    <reaction id="4" Reversible="No">
      <Equation>GO--&gt;Garomatics</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.028</velcons>
        <ActEner units="kJ/mol">95</ActEner>
      </Ratecoeff>
  </reactionData>

```

```

    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>Garomatics</Products>
  </reaction>
  <reaction id="5" Reversible="No">
    <Equation>Golefins--&gt;LPG</Equation>
    <Ratecoeff>
      <velcons units="s^-1">0.27</velcons>
      <ActEner units="kJ/mol">98</ActEner>
    </Ratecoeff>
    <Reactants>Golefins</Reactants>
    <Products>LPG</Products>
  </reaction>
  <reaction id="6" Reversible="No">
    <Equation>GO--&gt;coke</Equation>
    <Ratecoeff>
      <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.013</velcons>
      <ActEner units="kJ/mol">66</ActEner>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>coke</Products>
  </reaction>
  <reaction id="7" Reversible="No">
    <Equation>GO--&gt;Dry Gas</Equation>
    <Ratecoeff>
      <velcons units=" s^-1">3.0</velcons>
      <ActEner units="kJ/mol">190</ActEner>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>Dry Gas</Products>
  </reaction>
  <reaction id="8" Reversible="No">
    <Equation>GO--&gt;LPG</Equation>
    <Ratecoeff>
      <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.020</velcons>
      <ActEner units="kJ/mol">88</ActEner>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>LPG</Products>
  </reaction>
</reactionData>
</Mechanism6>
<Mechanism7>
  <Name>Bollas</Name>
  <Lumps>5</Lumps>
  <Year>2007</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <API units="">25.2</API>
      <TBP units="k">
        <IBP>539.3</IBP>
        <wt10>591.6</wt10>
        <wt30>658.5</wt30>
        <wt50>698.4</wt50>
        <wt70>726</wt70>
        <wt90>758.4</wt90>
        <FBP>782.4</FBP>
      </TBP>
      <sgravity units="-o-">0.903</sgravity>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Dry Gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>

```

```

</species4>
<species5 name="LPG">
  <density units="kg/m3">-0</density>
  <PesoM units="kg/kmol">-0</PesoM>
</species5>
</speciesData>
<reactionData id="reaction_data">
  <reaction id="1" Reversible="No">
    <Equation>GO--&gt;Gasoline</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.021</velcons>
      <ActEner units="kcal/gmol">7.46</ActEner>
      <Rate units="wtfrac^-1 s^-1">0.07<!--at 520°C--></Rate>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>Gasoline</Products>
  </reaction>
  <reaction id="2" Reversible="No">
    <Equation>GO--&gt;LPG</Equation>
    <Reactants>GO</Reactants>
    <Products>LPG</Products>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0057</velcons>
      <ActEner units="kcal/gmol">10.29</ActEner>
      <Rate units="wtfrac^-1 s^-1">0.11<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="3" Reversible="No">
    <Equation>GO--&gt;DG</Equation>
    <Reactants>GO</Reactants>
    <Products>DG</Products>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0013</velcons>
      <ActEner units="kcal/gmol">17.70</ActEner>
      <Rate units="wtfrac^-1 s^-1">2.83<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="4" Reversible="No">
    <Equation>GO--&gt;coke</Equation>
    <Reactants>GO</Reactants>
    <Products>coke</Products>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.007913</velcons>
      <ActEner units="kcal/gmol">2.87</ActEner>
      <Rate units="wtfrac^-1 s^-1">0.00014<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="5" Reversible="No">
    <Equation>Gne--&gt;LPG</Equation>
    <Reactants>Gne</Reactants>
    <Products>LPG</Products>
    <Ratecoeff>
      <velcons units=" s^-1">0.00085</velcons>
      <ActEner units="kcal/gmol">16.11</ActEner>
      <Rate units="1/s">22.82<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="6" Reversible="No">
    <Equation>Gne--&gt;DG</Equation>
    <Reactants>Gne</Reactants>
    <Products>DG</Products>
    <Ratecoeff>
      <velcons units="s^-1">0.000014</velcons>
      <ActEner units="kcal/gmol">26.77</ActEner>
      <Rate units="1/s">31.41<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="7" Reversible="No">
    <Equation>Gne--&gt;coke</Equation>
    <Reactants>Gne</Reactants>
    <Products>coke</Products>

```

```

    <Ratecoeff>
      <velcons units=" s^-1">0.00077</velcons>
      <ActEner units="kcal/gmol">3.33</ActEner>
      <Rate units="1/s">0.00632<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="8" Reversible="No">
    <Equation>LPG--&gt; coke</Equation>
    <Reactants>LPG</Reactants>
    <Products>coke</Products>
    <Ratecoeff>
      <velcons units="s^-1">0.00001</velcons>
      <ActEner units="kcal/gmol">23.60</ActEner>
      <Rate units="1/s">31.82<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
</reactionData>
</Mechanism7>
<Mechanism8>
  <Name>Barbosa</Name>
  <Lumps>11</Lumps>
  <Year>2013</Year>
  <speciesData id="species_data">
    <species1 name="Ph">
      <density units="kg/m3">900</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species1>
    <species2 name="Nh">
      <density units="kg/m3">850</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species2>
    <species3 name="Ah">
      <density units="kg/m3">875</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species3>
    <species4 name="Cah">
      <density units="kg/m3">880</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species4>
    <species5 name="P1">
      <density units="kg/m3">750</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species5>
    <species6 name="N1">
      <density units="kg/m3">775</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species6>
    <species7 name="A1">
      <density units="kg/m3">780</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species7>
    <species8 name="Ca1">
      <density units="kg/m3">715</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species8>
    <species9 name="Gas">
      <density units="kg/m3">100</density>
      <PesoM units="kg/kmol">50</PesoM>
    </species9>
    <species10 name="coque">
      <density units="kg/m3">1800</density>
      <PesoM units="kg/kmol">12</PesoM>
    </species10>
    <species11 name="Dry Gas">
      <density units="kg/m3">155</density>
      <PesoM units="kg/kmol">18.4</PesoM>
    </species11>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="01" Reversible="No">
      <Equation>Ph--&gt; P1</Equation>

```

```

<Ratecoeff>
  <ActEner units="Btu/lbmol">26100</ActEner>
  <Rate units="1/s">0.196<!--at 1000°F--></Rate>
  <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>Ph</Reactants>
<Products>P1</Products>
</reaction>
<reaction id="02" Reversible="No">
  <Equation>Nh--&gt;N1</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.196<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>N1</Products>
</reaction>
<reaction id="03" Reversible="No">
  <Equation>Ah--&gt;A1</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.196<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>A1</Products>
</reaction>
<reaction id="04" Reversible="No">
  <Equation>Ah--&gt;R1</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.489<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>R1</Products>
</reaction>
<reaction id="05" Reversible="No">
  <Equation>Rh--&gt;R1</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.049<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Rh</Reactants>
  <Products>R1</Products>
</reaction>
<reaction id="06" Reversible="No">
  <Equation>Ph--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.611<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="07" Reversible="No">
  <Equation>Nh--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.939<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="08" Reversible="No">
  <Equation>Ah--&gt;G</Equation>
  <Ratecoeff>

```

```

    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.685<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="09" Reversible="No">
  <Equation>Ph--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.099<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="10" Reversible="No">
  <Equation>Nh--&gt;Coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.149<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>Coque</Products>
</reaction>
<reaction id="11" Reversible="No">
  <Equation>Ah--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.198<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="12" Reversible="No">
  <Equation>Rh--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.149<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Rh</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="13" Reversible="No">
  <Equation>P1--&gt;g</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.282<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>P1</Reactants>
  <Products>g</Products>
</reaction>
<reaction id="14" Reversible="No">
  <Equation>N1--&gt;g</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.282<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>N1</Reactants>
  <Products>g</Products>
</reaction>
<reaction id="15" Reversible="No">
  <Equation>A1--&gt;g</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>

```



```

    <Rate units="1/s">0.196<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Al</Reactants>
  <Products>g</Products>
</reaction>
<reaction id="16" Reversible="No">
  <Equation>P1--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.099<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>P1</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="17" Reversible="No">
  <Equation>N1--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.099<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>N1</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="18" Reversible="No">
  <Equation>Al--&gt;c</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.050<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Al</Reactants>
  <Products>c</Products>
</reaction>
<reaction id="19" Reversible="No">
  <Equation>R1--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.01<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>R1</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="20" Reversible="No">
  <Equation>g--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">18000</ActEner>
    <Rate units="1/s">0.048<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>g</Reactants>
  <Products>coque</Products>
</reaction>
<reaction id="21" Reversible="No">
  <Equation>HFO--&gt;DG</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">18000</ActEner>
    <Rate units="1/s">0.048<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>HFO</Reactants>
  <Products>DG</Products>
</reaction>
<reaction id="22" Reversible="No">
  <Equation>LFO--&gt;DG</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">0.282</ActEner>
    <Rate units="1/s">0.060<!--at 1000°F--></Rate>

```

```

    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>LFO</Reactants>
  <Products>DG</Products>
</reaction>
<reaction id="23" Reversible="No">
  <Equation>g--&gt;DG</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">0.048</ActEner>
    <Rate units="1/s">0.042<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>g</Reactants>
  <Products>DG</Products>
</reaction>
<reaction id="24" Reversible="No">
  <Equation>coque--&gt;DG</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">0.048</ActEner>
    <Rate units="1/s">0.042<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>coque</Reactants>
  <Products>DG</Products>
</reaction>
</reactionData>
</Mechanism8>
<Mechanism9>
  <Name>Gianetto</Name>
  <Lumps>3</Lumps>
  <Year>1994</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <TBP units="k">
        <IBP>539.45</IBP>
        <wt5>573.15</wt5>
        <wt10>595</wt10>
        <wt30>630</wt30>
        <wt50>660</wt50>
        <wt70>696</wt70>
        <wt90>747</wt90>
        <wt95>771</wt95>
        <FBP>817</FBP>
      </TBP>
      <sgravity units="-o-">0.9389</sgravity>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="light gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>VGO--&gt;light gases</Equation>
      <Ratecoeff>
        <velcons units="m^6 kmol^-1 kgcat^-1 s^-1">941900000000</velcons>
        <ActEner units="cal/mol">22795.3</ActEner>
      </Ratecoeff>
      <Reactants>VGO</Reactants>
      <Products>light gases</Products>
    </reaction>
    <reaction id="2" Reversible="No">
      <Equation>VGO--&gt;Gasoline</Equation>

```

```

    <Ratecoeff>
      <velcons units="m^6 kmol^-1 kgcat^-1 s^-1">3769000000000000</velcons>
      <ActEner units="cal/mol">29900.5</ActEner>
    </Ratecoeff>
    <Reactants>VGO</Reactants>
    <Products>Gasoline</Products>
  </reaction>
  <reaction id="3" Reversible="No">
    <Equation>VGO--&gt;coke</Equation>
    <Ratecoeff>
      <velcons units="m^6 mol^-1 kgcat^-1 s^-1">107000000000000</velcons>
      <ActEner units="cal/mol">34824</ActEner>
    </Ratecoeff>
    <Reactants>VGO</Reactants>
    <Products>coke</Products>
  </reaction>
  <reaction id="4" Reversible="No">
    <Equation>Gasoline--&gt;gas+coke</Equation>
    <Ratecoeff>
      <velcons units="m^3 kgcat^-1 s^-1">1093</velcons>
      <ActEner units="cal/mol">11402.3</ActEner>
    </Ratecoeff>
    <Reactants>Gasoline</Reactants>
    <Products>gas+coke</Products>
  </reaction>
</reactionData>
</Mechanism9>
<Expresults>
  <ER1>
    <Name>Ali</Name>
    <Lumps></Lumps>
    <Year>1997</Year>
    <Feedproperties id="Properties">
      <IBP>NR</IBP>
      <FBP>NR</FBP>
      <MWVGO>350</MWVGO>
      <MWGNE>114</MWGNE>
      <MWLG>50</MWLG>
      <MWcoke>12</MWcoke>
    </Feedproperties>
    <Operationconditions id="reaction_data">
      <MOT>522</MOT>
      <ReactorLength>34.22</ReactorLength>
      <CTO>7.2</CTO>
      <RiserDiameter>0.8</RiserDiameter>
      <Feedrate>20</Feedrate>
    </Operationconditions>
    <Yields id="reaction_data">
      <VGO>0.27</VGO>
      <GNE>0.439</GNE>
      <LG>0.233</LG>
      <Coke>0.058</Coke>
    </Yields>
  </ER1>
  <ER2>
    <Name>Dasila</Name>
    <Lumps></Lumps>
    <Year>2012</Year>
    <Feedproperties id="Properties">
      <IBP>288</IBP>
      <FBP>546</FBP>
      <MWVGO>350</MWVGO>
      <MWGNE>114</MWGNE>
      <MWLG>50</MWLG>
      <MWcoke>12</MWcoke>
    </Feedproperties>
    <Operationconditions id="reaction_data">
      <MOT>500</MOT>
      <ReactorLength>36.965</ReactorLength>
      <CTO>6.4819</CTO>
      <RiserDiameter>0.684</RiserDiameter>

```

```
<Feedrate>32.14</Feedrate>
</Operationconditions>
<Yields id="reaction_data">
  <VGO>0.456</VGO>
  <GNE>0.34</GNE>
  <LG>0.158</LG>
  <Coke>0.046</Coke>
</Yields>
</ER2>
<ER3>
  <Name>Lopes</Name>
  <Year>2011</Year>
  <Feedproperties id="Properties">
    <IBP>NR</IBP>
    <FBP>NR</FBP>
    <MWVGO>400</MWVGO>
    <MWGNE>200</MWGNE>
    <MWLG>36</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>522</MOT>
    <ReactorLength>33</ReactorLength>
    <CTO>7</CTO>
    <RiserDiameter>0.8</RiserDiameter>
    <Feedrate>20</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.266</VGO>
    <GNE>0.478</GNE>
    <LG>0.182</LG>
    <Coke>0.071</Coke>
  </Yields>
</ER3>
<ER4>
  <Name>Dasila1</Name>
  <Year>2015</Year>
  <Feedproperties id="Properties">
    <IBP>288</IBP>
    <FBP>546</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>494.3</MOT>
    <ReactorLength>37</ReactorLength>
    <CTO>4.56</CTO>
    <RiserDiameter>0.7</RiserDiameter>
    <Feedrate>49.3</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.317</VGO>
    <GNE>0.515</GNE>
    <LG>0.129</LG>
    <Coke>0.04</Coke>
  </Yields>
</ER4>
<ER5>
  <Name>Dasila2</Name>
  <Year>2015</Year>
  <Feedproperties id="Properties">
    <IBP>268</IBP>
    <FBP>525</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
```

```

    <MOT>494.4</MOT>
    <ReactorLength>37</ReactorLength>
    <CTO>4.9960</CTO>
    <RiserDiameter>0.7</RiserDiameter>
    <Feedrate>50.2</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.285</VGO>
    <GNE>0.543</GNE>
    <LG>0.136</LG>
    <Coke>0.036</Coke>
  </Yields>
</ER5>
<ER6>
  <Name>Dasila3</Name>
  <Year>2015</Year>
  <Feedproperties id="Properties">
    <IBP>253</IBP>
    <FBP>526</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>494.4</MOT>
    <ReactorLength>37</ReactorLength>
    <CTO>5.092</CTO>
    <RiserDiameter>0.7</RiserDiameter>
    <Feedrate>46.7</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.26</VGO>
    <GNE>0.558</GNE>
    <LG>0.145</LG>
    <Coke>0.0037</Coke>
  </Yields>
</ER6>
<ER7>
  <Name>Dasila4</Name>
  <Year>2015</Year>
  <Feedproperties id="Properties">
    <IBP>282</IBP>
    <FBP>555</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>494.2</MOT>
    <ReactorLength>37</ReactorLength>
    <CTO>4.4872</CTO>
    <RiserDiameter>0.7</RiserDiameter>
    <Feedrate>47.2</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.347</VGO>
    <GNE>0.486</GNE>
    <LG>0.125</LG>
    <Coke>0.037</Coke>
  </Yields>
</ER7>
<ER8>
  <Name>Frag</Name>
  <Year>1994</Year>
  <Feedproperties id="Properties">
    <IBP>NR</IBP>
    <FBP>NR</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>

```

```

    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>476</MOT>
    <ReactorLength>34.2</ReactorLength>
    <CTO>7</CTO>
    <RiserDiameter>0.8</RiserDiameter>
    <Feedrate>25</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.309</VGO>
    <GNE>0.49</GNE>
    <LG>0.148</LG>
    <Coke>0.053</Coke>
  </Yields>
</ER8>
<ER9>
  <Name>Chang1</Name>
  <Year>2012</Year>
  <Feedproperties id="Properties">
    <IBP>305</IBP>
    <FBP>498</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>520</MOT>
    <ReactorLength>41.1</ReactorLength>
    <CTO>8.1</CTO>
    <RiserDiameter>1.5</RiserDiameter>
    <Feedrate>34.611</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.3181</VGO>
    <GNE>0.402</GNE>
    <LG>0.2045</LG>
    <Coke>0.0754</Coke>
  </Yields>
</ER9>
<ER10>
  <Name>Chang2</Name>
  <Year>2012</Year>
  <Feedproperties id="Properties">
    <IBP>305</IBP>
    <FBP>498</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>520</MOT>
    <ReactorLength>41.1</ReactorLength>
    <CTO>6</CTO>
    <RiserDiameter>1.5</RiserDiameter>
    <Feedrate>34.611</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.3361</VGO>
    <GNE>0.3914</GNE>
    <LG>0.1965</LG>
    <Coke>0.076</Coke>
  </Yields>
</ER10>
<ER11>
  <Name>Baudrex</Name>
  <Year>2010</Year>
  <Feedproperties id="Properties">

```

```

    <IBP>NR</IBP>
    <FBP>NR</FBP>
    <MWVGO>382</MWVGO>
    <MWGNE>120</MWGNE>
    <MWLG>45</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>527</MOT>
    <ReactorLength>27.5</ReactorLength>
    <CTO>3.7</CTO>
    <RiserDiameter>0.4</RiserDiameter>
    <Feedrate>2.68</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.592</VGO>
    <GNE>0.297</GNE>
    <LG>0.078</LG>
    <Coke>0.033</Coke>
  </Yields>
</ER11>
<ER12>
  <Name>Ecopetrol</Name>
  <Year>2014</Year>
  <Feedproperties id="Properties">
    <IBP>218</IBP>
    <FBP>566</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="reaction_data">
    <MOT>563</MOT>
    <ReactorLength>39.59</ReactorLength>
    <CTO>8.62</CTO>
    <RiserDiameter>1.34</RiserDiameter>
    <Feedrate>60.1297</Feedrate>
  </Operationconditions>
  <Yields id="reaction_data">
    <VGO>0.386</VGO>
    <GNE>0.394</GNE>
    <LG>0.157</LG>
    <Coke>0.059</Coke>
  </Yields>
</ER12>
</Expresults>
</FCC>
<Hydrocracking>
  <Mechanism1>
    <Name>Qader</Name>
    <Lumps>2</Lumps>
    <Year>1969</Year>
    <speciesData id="species_data">
      <species1 name="SVG0">
        <API units="-o-">31.80</API>
        <sgravity units="-o-">0.8665</sgravity>
        <TBP units="K">
          <IBP>573</IBP>
          <wt50>615</wt50>
          <wt90>679</wt90>
          <FBP>703</FBP>
        </TBP>
      </species1>
      <species2 name="products">
        <density units="kg/m3">-0</density>
        <PesoM units="kg/kmol">-0</PesoM>
      </species2>
    </speciesData>
    <reactionData id="reaction_data">
      <reaction id="1" Reversible="No">

```

```

    <Equation>VGO--&gt;Products</Equation>
    <Ratecoeff>
      <ActEner units="kcal/mol">21.1</ActEner>
      <RC units="1/S">4273</RC>
    </Ratecoeff>
    <Reactants>VGO</Reactants>
    <Products>Products</Products>
  </reaction>
</reactionData>
</Mechanism1>
<Mechanism2>
  <Name>Orochko</Name>
  <Lumps>4</Lumps>
  <Year>1970</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="MD">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="Gases">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>VGO--&gt;MD</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.024</velcons>
        <ActEner units="kJ/mol">75</ActEner>
      </Ratecoeff>
      <Reactants>VGO</Reactants>
      <Products>MD</Products>
    </reaction>
    <reaction id="2" Reversible="No">
      <Equation>VGO--&gt;Gasoline</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.044</velcons>
        <ActEner units="kJ/mol">106</ActEner>
      </Ratecoeff>
      <Reactants>VGO</Reactants>
      <Products>Gasoline</Products>
    </reaction>
    <reaction id="3" Reversible="No">
      <Equation>VGO--&gt;Gases</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.009</velcons>
        <ActEner units="kJ/mol">68</ActEner>
      </Ratecoeff>
      <Reactants>VGO</Reactants>
      <Products>Gases</Products>
    </reaction>
  </reactionData>
</Mechanism2>
<Mechanism3>
  <Name>AboulGheit</Name>
  <Lumps>4</Lumps>
  <Year>1989</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>

```



```

<species2 name="MD">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species2>
<species3 name="Gasoline">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species3>
<species4 name="Gases">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species4>
</speciesData>
<reactionData id="reaction_data">
  <reaction1 id="1" Reversible="No">
    <Equation>VGO--&gt;MD</Equation>
    <Ratecoeff>
      <velcons>
        <T400 Units="1/h">0.286</T400>
        <T425 Units="1/h">0.500</T425>
        <T450 Units="1/h">0.688</T450>
      </velcons>
      <ActEner units="kcal/mol">17.51</ActEner>
    </Ratecoeff>
    <Reactants>VGO</Reactants>
    <Products>MD</Products>
  </reaction1>
  <reaction2 id="2" Reversible="No">
    <Equation>VGO--&gt;Gasoline</Equation>
    <Ratecoeff>
      <velcons>
        <T400 Units="1/h">0.040</T400>
        <T425 Units="1/h">0.083</T425>
        <T450 Units="1/h">0.140</T450>
      </velcons>
      <ActEner units="kcal/mol">24.02</ActEner>
    </Ratecoeff>
    <Reactants>VGO</Reactants>
    <Products>Gasoline</Products>
  </reaction2>
  <reaction3 id="3" Reversible="No">
    <Equation>VGO--&gt;Gases</Equation>
    <Ratecoeff>
      <velcons>
        <T400 Units="1/h">0.026</T400>
        <T425 Units="1/h">0.048</T425>
        <T450 Units="1/h">0.069</T450>
      </velcons>
      <ActEner units="kcal/mol">18.67</ActEner>
    </Ratecoeff>
    <Reactants>VGO</Reactants>
    <Products>Gases</Products>
  </reaction3>
</reactionData>
</Mechanism3>
<Mechanism4>
  <Name>Krishna</Name>
  <Lumps>6</Lumps>
  <Year>1989</Year>
  <speciesData id="species_data">
    <species1 name="Sulfur Compounds">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species1>
    <species2 name="Ah">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species2>
    <species3 name="Nh">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species3>
  </speciesData>

```

```

</species3>
<species4 name="Ph">
  <density units="kg/m3">-0</density>
  <PesoM units="kg/kmol">-0</PesoM>
</species4>
<species5 name="Al">
  <density units="kg/m3">-0</density>
  <PesoM units="kg/kmol">-0</PesoM>
</species5>
<species6 name="Nl">
  <density units="kg/m3">-0</density>
  <PesoM units="kg/kmol">-0</PesoM>
</species6>
<species7 name="Pl">
  <density units="kg/m3">-0</density>
  <PesoM units="kg/kmol">-0</PesoM>
</species7>
</speciesData>
<reactionData id="reaction_data">
  <reaction1 id="1" Reversible="No">
    <Equation>sulfur Compounds--&gt;Ah</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">8.3</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>sulfur Compounds</Reactants>
    <Products>Ah</Products>
  </reaction1>
  <reaction2 id="2" Reversible="No">
    <Equation>Ah--&gt;Nh</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">1.2633</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Nh</Products>
  </reaction2>
  <reaction3 id="3" Reversible="No">
    <Equation>Ah--&gt;Al</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.6042</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Al</Products>
  </reaction3>
  <reaction4 id="4" Reversible="No">
    <Equation>Ah--&gt;Ph</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.0421</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Ph</Products>
  </reaction4>
  <reaction5 id="5" Reversible="No">
    <Equation>Ah--&gt;Pl</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.5309</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Pl</Products>
  </reaction5>
  <reaction6 id="6" Reversible="No">
    <Equation>Ah--&gt;Nl</Equation>

```

```

    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.0397</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Nl</Products>
  </reaction6>
  <reaction7 id="7" Reversible="No">
    <Equation>Nh--&gt;Nl</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">1.1855</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Nh</Reactants>
    <Products>Nl</Products>
  </reaction7>
  <reaction8 id="8" Reversible="No">
    <Equation>Nh--&gt;P1</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.1619</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Nh</Reactants>
    <Products>P1</Products>
  </reaction8>
  <reaction9 id="9" Reversible="No">
    <Equation>Ph--&gt;P1</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.4070</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ph</Reactants>
    <Products>P1</Products>
  </reaction9>
  <reaction10 id="10" Reversible="No">
    <Equation>Al--&gt;Nl</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.2909</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Al</Reactants>
    <Products>Nl</Products>
  </reaction10>
  <reaction11 id="11" Reversible="No">
    <Equation>Nl--&gt;P1</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.0818</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Nl</Reactants>
    <Products>P1</Products>
  </reaction11>
</reactionData>
</Mechanism4>
<Mechanism5>
  <Name>Mosby</Name>
  <Lumps>7</Lumps>
  <Year>1997</Year>
</Mechanism5>
<Mechanism6>
  <Name>Callejas</Name>
  <Lumps>3</Lumps>
  <Year>1999</Year>
<speciesData id="species_data">
  <species1 name="AR">

```

```

    <density units="kg/m3">-0-</density>
    <PesoM units="kg/kmol">-0-</PesoM>
  </species1>
  <species2 name="LO">
    <density units="kg/m3">-0-</density>
    <PesoM units="kg/kmol">-0-</PesoM>
  </species2>
  <species3 name="Gas">
    <density units="kg/m3">-0-</density>
    <PesoM units="kg/kmol">-0-</PesoM>
  </species3>
</speciesData>
<reactionData id="reaction_data">
  <reaction1 id="1" Reversible="No">
    <Equation>AR--&gt; ; LO</Equation>
    <Ratecoeff>
      <velcons>
        <T375 Units="L/gcath">0.30</T375>
        <T400 Units="L/gcath">0.46</T400>
        <T415 Units="L/gcath">1.45</T415>
      </velcons>
      <ActEner units="kcal/gmol">32.57</ActEner>
    </Ratecoeff>
    <Reactants>AR</Reactants>
    <Products>LO</Products>
  </reaction1>
  <reaction2 id="2" Reversible="No">
    <Equation>Ah--&gt; ; Nh</Equation>
    <Ratecoeff>
      <velcons>
        <T375 Units="L/gcath">0.79</T375>
        <T400 Units="L/gcath">2.72</T400>
        <T415 Units="L/gcath">5.77</T415>
      </velcons>
      <ActEner units="kcal/gmol">43.90</ActEner>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Nh</Products>
  </reaction2>
</reactionData>
</Mechanism6>
<Mechanism7>
  <Name>Botchwey1</Name>
  <Lumps>6</Lumps>
  <Year>2003</Year>
  <speciesData id="species_data">
    <species1 name="A">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species1>
    <species2 name="B">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species2>
    <species3 name="C">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species3>
    <species4 name="D">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction1 id="1" Reversible="No">
      <Equation>AR--&gt; ; LO</Equation>
      <Ratecoeff>
        <velcons>
          <T340 Units="h-1">0.064</T340>
          <T350 Units="h-1">0.1</T350>
          <T360 Units="h-1">0.164</T360>
        </velcons>
      </Ratecoeff>
    </reaction1>
  </reactionData>

```

```

    <T370 Units="h-1">0.229</T370>
  </velcons>
  <ActEner units="kJ/mol">32.57</ActEner>
</Ratecoeff>
<Reactants>AR</Reactants>
<Products>LO</Products>
</reaction1>
<reaction2 id="2" Reversible="No">
  <Equation>Ah--&gt;Nh</Equation>
  <Ratecoeff>
    <velcons>
      <T340 Units="h-1">0.016</T340>
      <T350 Units="h-1">0.032</T350>
      <T360 Units="h-1">0.053</T360>
      <T370 Units="h-1">0.076</T370>
    </velcons>
    <ActEner units="kJ/mol">168</ActEner>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>Nh</Products>
</reaction2>
<reaction3 id="1" Reversible="No">
  <Equation>AR--&gt;LO</Equation>
  <Ratecoeff>
    <velcons>
      <T340 Units="h-1">0.147</T340>
      <T350 Units="h-1">0.163</T350>
      <T360 Units="h-1">0.184</T360>
      <T370 Units="h-1">0.207</T370>
    </velcons>
    <ActEner units="kJ/gmol">37</ActEner>
  </Ratecoeff>
  <Reactants>AR</Reactants>
  <Products>LO</Products>
</reaction3>
</reactionData>
</Mechanism7>
<Mechanism7II>
  <Name>Botchwey2</Name>
  <Lumps>6</Lumps>
  <Year>2003</Year>
  <speciesData id="species_data">
    <species1 name="A">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="B">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="C">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="D">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction1 id="1" Reversible="No">
      <Equation>AR--&gt;LO</Equation>
      <Ratecoeff>
        <velcons>
          <T370 Units="h-1">0.229</T370>
          <T380 Units="h-1">0.299</T380>
          <T390 Units="h-1">0.393</T390>
          <T400 Units="h-1">0.531</T400>
        </velcons>
        <ActEner units="kJ/mol">101</ActEner>
      </Ratecoeff>

```

```

    <Reactants>AR</Reactants>
    <Products>LO</Products>
  </reaction1>
  <reaction2 id="2" Reversible="No">
    <Equation>Ah--&gt;Nh</Equation>
    <Ratecoeff>
      <velcons>
        <T370 Units="h-1">0.116</T370>
        <T380 Units="h-1">0.148</T380>
        <T390 Units="h-1">0.186</T390>
        <T400 Units="h-1">0.242</T400>
      </velcons>
      <ActEner units="kJ/mol">88</ActEner>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Nh</Products>
  </reaction2>
  <reaction3 id="1" Reversible="No">
    <Equation>AR--&gt;LO</Equation>
    <Ratecoeff>
      <velcons>
        <T370 Units="h-1">0.167</T370>
        <T380 Units="h-1">0.199</T380>
        <T390 Units="h-1">0.237</T390>
        <T400 Units="h-1">0.293</T400>
      </velcons>
      <ActEner units="kJ/mol">67</ActEner>
    </Ratecoeff>
    <Reactants>AR</Reactants>
    <Products>LO</Products>
  </reaction3>
  <reaction4 id="1" Reversible="No">
    <Equation>AR--&gt;LO</Equation>
    <Ratecoeff>
      <velcons>
        <T370 Units="h-1">0.050</T370>
        <T380 Units="h-1">0.070</T380>
        <T390 Units="h-1">0.101</T390>
        <T400 Units="h-1">0.229</T400>
      </velcons>
      <ActEner units="kJ/mol">133</ActEner>
    </Ratecoeff>
    <Reactants>AR</Reactants>
    <Products>LO</Products>
  </reaction4>
</reactionData>
</Mechanism7II>
<Mechanism7III>
  <Name>Botchwey1</Name>
  <Lumps>6</Lumps>
  <Year>2003</Year>
  <speciesData id="species_data">
    <species1 name="A">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="B">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="C">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="D">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction1 id="1" Reversible="No">

```

```

<Equation>AR--&gt;LO</Equation>
<Ratecoeff>
  <velcons>
    <T400 Units="h-1">0.195</T400>
    <T410 Units="h-1">0.259</T410>
    <T420 Units="h-1">0.334</T420>
  </velcons>
  <ActEner units="kJ/mol">107</ActEner>
</Ratecoeff>
<Reactants>AR</Reactants>
<Products>LO</Products>
</reaction1>
<reaction2 id="2" Reversible="No">
<Equation>Ah--&gt;Nh</Equation>
<Ratecoeff>
  <velcons>
    <T400 Units="h-1">0.201</T400>
    <T410 Units="h-1">0.276</T410>
    <T420 Units="h-1">0.357</T420>
  </velcons>
  <ActEner units="kJ/mol">111</ActEner>
</Ratecoeff>
<Reactants>Ah</Reactants>
<Products>Nh</Products>
</reaction2>
<reaction3 id="1" Reversible="No">
<Equation>AR--&gt;LO</Equation>
<Ratecoeff>
  <velcons>
    <T400 Units="h-1">0.252</T400>
    <T410 Units="h-1">0.327</T410>
    <T420 Units="h-1">0.408</T420>
  </velcons>
  <ActEner units="kJ/mol">67</ActEner>
</Ratecoeff>
<Reactants>AR</Reactants>
<Products>LO</Products>
</reaction3>
<reaction4 id="1" Reversible="No">
<Equation>AR--&gt;LO</Equation>
<Ratecoeff>
  <velcons>
    <T400 Units="h-1">0.151</T400>
    <T410 Units="h-1">0.220</T410>
    <T420 Units="h-1">0.293</T420>
  </velcons>
  <ActEner units="kJ/mol">122</ActEner>
</Ratecoeff>
<Reactants>AR</Reactants>
<Products>LO</Products>
</reaction4>
<reaction5 id="1" Reversible="No">
<Equation>AR--&gt;LO</Equation>
<Ratecoeff>
  <velcons>
    <T400 Units="h-1">0.169</T400>
    <T410 Units="h-1">0.233</T410>
    <T420 Units="h-1">0.308</T420>
  </velcons>
  <ActEner units="kJ/mol">119</ActEner>
</Ratecoeff>
<Reactants>AR</Reactants>
<Products>LO</Products>
</reaction5>
</reactionData>
</Mechanism7III>
<Mechanism8>
  <Name>Aoyagi</Name>
  <Lumps>3</Lumps>
  <Year>2003</Year>
  <speciesData id="species_data">

```

```

<species1 name="Sulfur Compounds">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species1>
<species2 name="Ah">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species2>
<species3 name="Nh">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species3>
<species4 name="Ph">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species4>
<species5 name="Al">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species5>
<species6 name="Nl">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species6>
<species7 name="Pl">
  <density units="kg/m3">-0-</density>
  <PesoM units="kg/kmol">-0-</PesoM>
</species7>
</speciesData>
<reactionData id="reaction_data">
  <reaction1 id="1" Reversible="No">
    <Equation>sulfur Compounds--&gt;Ah</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">8.3</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>sulfur Compounds</Reactants>
    <Products>Ah</Products>
  </reaction1>
  <reaction2 id="2" Reversible="No">
    <Equation>Ah--&gt;Nh</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">1.2633</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Nh</Products>
  </reaction2>
  <reaction3 id="3" Reversible="No">
    <Equation>Ah--&gt;Al</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.6042</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Al</Products>
  </reaction3>
  <reaction4 id="4" Reversible="No">
    <Equation>Ah--&gt;Ph</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.0421</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Ph</Products>
  </reaction4>
  <reaction5 id="5" Reversible="No">

```



```

<Equation>Ah--&gt;P1</Equation>
<Ratecoeff>
  <velcons>
    <T371 Units="1/h">0.5309</T371>
  </velcons>
</Ratecoeff>
<Reactants>Ah</Reactants>
<Products>P1</Products>
</reaction5>
<reaction6 id="6" Reversible="No">
  <Equation>Ah--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.0397</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>N1</Products>
</reaction6>
<reaction7 id="7" Reversible="No">
  <Equation>Nh--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">1.1855</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>N1</Products>
</reaction7>
<reaction8 id="8" Reversible="No">
  <Equation>Nh--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.1619</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>P1</Products>
</reaction8>
<reaction9 id="9" Reversible="No">
  <Equation>Ph--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.4070</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>P1</Products>
</reaction9>
<reaction10 id="10" Reversible="No">
  <Equation>A1--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.2909</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>A1</Reactants>
  <Products>N1</Products>
</reaction10>
<reaction11 id="11" Reversible="No">
  <Equation>N1--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.0818</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>N1</Reactants>
  <Products>P1</Products>
</reaction11>
</reactionData>
</Mechanism8>

```

```

<Mechanism9>
  <Name>Sánchez</Name>
  <Lumps>5</Lumps>
  <Year>2003</Year>
  <speciesData id="species_data">
    <species1 name="Sulfur Compounds">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="Ah">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Nh">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="Ph">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
    <species5 name="Al">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species5>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction1 id="1" Reversible="No">
      <Equation>sulfur Compounds--&gt;Ah</Equation>
      <Ratecoeff>
        <velcons>
          <T371 Units="1/h">8.3</T371>
        </velcons>
      </Ratecoeff>
      <Reactants>sulfur Compounds</Reactants>
      <Products>Ah</Products>
    </reaction1>
    <reaction2 id="2" Reversible="No">
      <Equation>Ah--&gt;Nh</Equation>
      <Ratecoeff>
        <velcons>
          <T371 Units="1/h">1.2633</T371>
        </velcons>
      </Ratecoeff>
      <Reactants>Ah</Reactants>
      <Products>Nh</Products>
    </reaction2>
    <reaction3 id="3" Reversible="No">
      <Equation>Ah--&gt;Al</Equation>
      <Ratecoeff>
        <velcons>
          <T371 Units="1/h">0.6042</T371>
        </velcons>
      </Ratecoeff>
      <Reactants>Ah</Reactants>
      <Products>Al</Products>
    </reaction3>
    <reaction4 id="4" Reversible="No">
      <Equation>Ah--&gt;Ph</Equation>
      <Ratecoeff>
        <velcons>
          <T371 Units="1/h">0.0421</T371>
        </velcons>
      </Ratecoeff>
      <Reactants>Ah</Reactants>
      <Products>Ph</Products>
    </reaction4>
    <reaction5 id="5" Reversible="No">
      <Equation>Ah--&gt;Pl</Equation>
      <Ratecoeff>
        <velcons>

```

```

    <T371 Units="1/h">0.5309</T371>
  </velcons>
</Ratecoeff>
<Reactants>Ah</Reactants>
<Products>P1</Products>
</reaction5>
<reaction6 id="6" Reversible="No">
  <Equation>Ah--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.0397</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>N1</Products>
</reaction6>
<reaction7 id="7" Reversible="No">
  <Equation>Nh--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">1.1855</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>N1</Products>
</reaction7>
<reaction8 id="8" Reversible="No">
  <Equation>Nh--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.1619</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>P1</Products>
</reaction8>
<reaction9 id="9" Reversible="No">
  <Equation>Ph--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.4070</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>P1</Products>
</reaction9>
<reaction10 id="10" Reversible="No">
  <Equation>Al--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.2909</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Al</Reactants>
  <Products>N1</Products>
</reaction10>
<reaction11 id="11" Reversible="No">
  <Equation>N1--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.0818</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>N1</Reactants>
  <Products>P1</Products>
</reaction11>
</reactionData>
</Mechanism9>
<Mechanism10>
  <Name>Botchwey2</Name>
  <Lumps>4</Lumps>

```

```

<Year>2004</Year>
<speciesData id="species_data">
  <species1 name="Sulfur Compounds">
    <density units="kg/m3">-0</density>
    <PesoM units="kg/kmol">-0</PesoM>
  </species1>
  <species2 name="Ah">
    <density units="kg/m3">-0</density>
    <PesoM units="kg/kmol">-0</PesoM>
  </species2>
  <species3 name="Nh">
    <density units="kg/m3">-0</density>
    <PesoM units="kg/kmol">-0</PesoM>
  </species3>
  <species4 name="Ph">
    <density units="kg/m3">-0</density>
    <PesoM units="kg/kmol">-0</PesoM>
  </species4>
  <species5 name="Al">
    <density units="kg/m3">-0</density>
    <PesoM units="kg/kmol">-0</PesoM>
  </species5>
  <species6 name="N1">
    <density units="kg/m3">-0</density>
    <PesoM units="kg/kmol">-0</PesoM>
  </species6>
  <species7 name="P1">
    <density units="kg/m3">-0</density>
    <PesoM units="kg/kmol">-0</PesoM>
  </species7>
</speciesData>
<reactionData id="reaction_data">
  <reaction1 id="1" Reversible="No">
    <Equation>sulfur Compounds--&gt;Ah</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">8.3</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>sulfur Compounds</Reactants>
    <Products>Ah</Products>
  </reaction1>
  <reaction2 id="2" Reversible="No">
    <Equation>Ah--&gt;Nh</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">1.2633</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Nh</Products>
  </reaction2>
  <reaction3 id="3" Reversible="No">
    <Equation>Ah--&gt;Al</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.6042</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Al</Products>
  </reaction3>
  <reaction4 id="4" Reversible="No">
    <Equation>Ah--&gt;Ph</Equation>
    <Ratecoeff>
      <velcons>
        <T371 Units="1/h">0.0421</T371>
      </velcons>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>Ph</Products>
  </reaction4>
</reactionData>

```

```
</reaction4>
<reaction5 id="5" Reversible="No">
  <Equation>Ah--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.5309</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>P1</Products>
</reaction5>
<reaction6 id="6" Reversible="No">
  <Equation>Ah--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.0397</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>N1</Products>
</reaction6>
<reaction7 id="7" Reversible="No">
  <Equation>Nh--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">1.1855</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>N1</Products>
</reaction7>
<reaction8 id="8" Reversible="No">
  <Equation>Nh--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.1619</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>P1</Products>
</reaction8>
<reaction9 id="9" Reversible="No">
  <Equation>Ph--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.4070</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>P1</Products>
</reaction9>
<reaction10 id="10" Reversible="No">
  <Equation>A1--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.2909</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>A1</Reactants>
  <Products>N1</Products>
</reaction10>
<reaction11 id="11" Reversible="No">
  <Equation>N1--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.0818</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>N1</Reactants>
  <Products>P1</Products>
</reaction11>
```

```

</reactionData>
</Mechanism10>
<Mechanism11>
  <Name>Martinez</Name>
  <Lumps>5</Lumps>
  <Year>2012</Year>
  <speciesData id="species_data">
    <species1 name="Sulfur Compounds">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="Ah">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Nh">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="Ph">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
    <species5 name="Al">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species5>
    <species6 name="Nl">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species6>
    <species7 name="Pl">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species7>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction1 id="1" Reversible="No">
      <Equation>sulfur Compounds--&gt;Ah</Equation>
      <Ratecoeff>
        <velcons>
          <T371 Units="1/h">8.3</T371>
        </velcons>
      </Ratecoeff>
      <Reactants>sulfur Compounds</Reactants>
      <Products>Ah</Products>
    </reaction1>
    <reaction2 id="2" Reversible="No">
      <Equation>Ah--&gt;Nh</Equation>
      <Ratecoeff>
        <velcons>
          <T371 Units="1/h">1.2633</T371>
        </velcons>
      </Ratecoeff>
      <Reactants>Ah</Reactants>
      <Products>Nh</Products>
    </reaction2>
    <reaction3 id="3" Reversible="No">
      <Equation>Ah--&gt;Al</Equation>
      <Ratecoeff>
        <velcons>
          <T371 Units="1/h">0.6042</T371>
        </velcons>
      </Ratecoeff>
      <Reactants>Ah</Reactants>
      <Products>Al</Products>
    </reaction3>
    <reaction4 id="4" Reversible="No">
      <Equation>Ah--&gt;Ph</Equation>
      <Ratecoeff>
        <velcons>

```

```

    <T371 Units="1/h">0.0421</T371>
  </velcons>
</Ratecoeff>
<Reactants>Ah</Reactants>
<Products>Ph</Products>
</reaction4>
<reaction5 id="5" Reversible="No">
  <Equation>Ah--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.5309</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>P1</Products>
</reaction5>
<reaction6 id="6" Reversible="No">
  <Equation>Ah--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.0397</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>N1</Products>
</reaction6>
<reaction7 id="7" Reversible="No">
  <Equation>Nh--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">1.1855</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>N1</Products>
</reaction7>
<reaction8 id="8" Reversible="No">
  <Equation>Nh--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.1619</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>P1</Products>
</reaction8>
<reaction9 id="9" Reversible="No">
  <Equation>Ph--&gt;P1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.4070</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>P1</Products>
</reaction9>
<reaction10 id="10" Reversible="No">
  <Equation>A1--&gt;N1</Equation>
  <Ratecoeff>
    <velcons>
      <T371 Units="1/h">0.2909</T371>
    </velcons>
  </Ratecoeff>
  <Reactants>A1</Reactants>
  <Products>N1</Products>
</reaction10>
</reactionData>
</Mechanism11>
<Validationresults>
  <VR1>
    <Name>Mohanty</Name>

```

```

<Lumps></Lumps>
<Year>1992</Year>
<Feedproperties id="Properties">
  <IBP>NR</IBP>
  <FBP>NR</FBP>
  <MWVGO>350</MWVGO>
  <MWGNE>114</MWGNE>
  <MWLG>50</MWLG>
  <MWcoke>12</MWcoke>
</Feedproperties>
<Operationconditions id="reaction_data">
  <MOT>410</MOT>
  <ReactorLength>17.8</ReactorLength>
  <Feedrate>41.667</Feedrate>
</Operationconditions>
<Yields>
  <VGO>0.6289</VGO>
  <Distillates>0.2932</Distillates>
  <Naphtha>0.0629</Naphtha>
  <Gases>0.0157</Gases>
</Yields>
</VR1>
<VR2>
  <Name>Sadighi</Name>
  <Year>2003</Year>
  <Feedproperties id="Properties">
    <IBP>NR</IBP>
    <FBP>NR</FBP>
    <MWVGO>350</MWVGO>
    <MWGNE>114</MWGNE>
    <MWLG>50</MWLG>
    <MWcoke>12</MWcoke>
  </Feedproperties>
  <Operationconditions id="Operation conditions">
    <LHSV1>0<T1>360<Yields><VGO>1</VGO><Distillates>0</Distillates><Naphtha>0</Naphtha><Gases>0</Gases></Yields></T1><T2>370<Yields><VGO>1</VGO><Distillates>0</Distillates><Naphtha>0</Naphtha><Gases>0</Gases></Yields></T2><T3>380<Yields><VGO>1</VGO><Distillates>0</Distillates><Naphtha>0</Naphtha><Gases>0</Gases></Yields></T3><T4>390<Yields><VGO>1</VGO><Distillates>0</Distillates><Naphtha>0</Naphtha><Gases>0</Gases></Yields></T4></LHSV1>
    <LHSV2>0.9523<T1>360<Yields><VGO>0.7324</VGO><Distillates>0.1866</Distillates><Naphtha>0.0558</Naphtha><Gases>0.0117</Gases></Yields></T1><T2>370<Yields><VGO>0.7063</VGO><Distillates>0.1993</Distillates><Naphtha>0.0682</Naphtha><Gases>0.013</Gases></Yields></T2><T3>380<Yields><VGO>0.6755</VGO><Distillates>0.2139</Distillates><Naphtha>0.0823</Naphtha><Gases>0.0164</Gases></Yields></T3><T4>390<Yields><VGO>0.6208</VGO><Distillates>0.2456</Distillates><Naphtha>0.1028</Naphtha><Gases>0.0199</Gases></Yields></T4></LHSV2>
    <LHSV3>1.111<T1>360<Yields><VGO>0.7147</VGO><Distillates>0.1984</Distillates><Naphtha>0.0596</Naphtha><Gases>0.0137</Gases></Yields></T1><T2>370<Yields><VGO>0.6833</VGO><Distillates>0.2091</Distillates><Naphtha>0.0791</Naphtha><Gases>0.0161</Gases></Yields></T2><T3>380<Yields><VGO>0.6422</VGO><Distillates>0.2296</Distillates><Naphtha>0.0956</Naphtha><Gases>0.0223</Gases></Yields></T3><T4>390<Yields><VGO>0.5655</VGO><Distillates>0.2765</Distillates><Naphtha>0.1217</Naphtha><Gases>0.0286</Gases></Yields></T4></LHSV3>
    <LHSV4>1.25<T1>360<Yields><VGO>0.6753</VGO><Distillates>0.2233</Distillates><Naphtha>0.0713</Naphtha><Gases>0.0171</Gases></Yields></T1><T2>370<Yields><VGO>0.6312</VGO><Distillates>0.2441</Distillates><Naphtha>0.0892</Naphtha><Gases>0.0254</Gases></Yields></T2><T3>380<Yields><VGO>0.5767</VGO><Distillates>0.2677</Distillates><Naphtha>0.1196</Naphtha><Gases>0.0281</Gases></Yields></T3><T4>390<Yields><VGO>0.5094</VGO><Distillates>0.3155</Distillates><Naphtha>0.1393</Naphtha><Gases>0.0323</Gases></Yields></T4></LHSV4>
  </Operationconditions>
</VR2>
<VR3>
  <Name>Ali</Name>
  <Year>1997</Year>
  <Feedproperties id="Properties">

```



```

<IBP>NR</IBP>
<FBP>NR</FBP>
<MWVGO>350</MWVGO>
<MWGNE>114</MWGNE>
<MWLG>50</MWLG>
<MWcoke>12</MWcoke>
</Feedproperties>
<Operationconditions id="Operation conditions">

<LHSV1>0<T1>380<Yields><VGO>1</VGO><Distillates>0</Distillates><Naphtha>0</Naphtha><
Gases>0</Gases></Yields></T1><T2>395<Yields><VGO>1</VGO><Distillates>0</Distillates>
<Naphtha>0</Naphtha><Gases>0</Gases></Yields></T2><T3>410<Yields><VGO>1</VGO><Distil
lates>0</Distillates><Naphtha>0</Naphtha><Gases>0</Gases></Yields></T3></LHSV1>

<LHSV2>0.9009<T1>410<Yields><VGO>0.521</VGO><Distillates>0.358</Distillates><Naphtha
>0.103</Naphtha><Gases>0.016</Gases></Yields></T1></LHSV2>

<LHSV3>0.9524<T1>395<Yields><VGO>0.72</VGO><Distillates>0.232</Distillates><Naphtha>
0.041</Naphtha><Gases>0.008</Gases></Yields></T1><T2>410<Yields><VGO>0.506</VGO><Dis
tillates>0.374</Distillates><Naphtha>0.104</Naphtha><Gases>0.018</Gases></Yields></T
2></LHSV3>

<LHSV4>1<T1>380<Yields><VGO>0.795</VGO><Distillates>0.178</Distillates><Naphtha>0.02
3</Naphtha><Gases>0.004</Gases></Yields></T1></LHSV4>

<LHSV5>1.0309<T1>380<Yields><VGO>0.787</VGO><Distillates>0.19</Distillates><Naphtha>
0.019</Naphtha><Gases>0.0042</Gases></Yields></T1></LHSV5>

<LHSV6>1.0417<T1>395<Yields><VGO>0.696</VGO><Distillates>0.248</Distillates><Naphtha
>0.047</Naphtha><Gases>0.009</Gases></Yields></T1></LHSV6>
</Operationconditions>
</VR3>
<VR4>
<Name>AboulGheit</Name>
<Year>2003</Year>
<Feedproperties id="Properties">
<IBP>NR</IBP>
<FBP>NR</FBP>
<MWVGO>350</MWVGO>
<MWGNE>114</MWGNE>
<MWLG>50</MWLG>
<MWcoke>12</MWcoke>
</Feedproperties>
<Operationconditions id="Operation conditions">

<LHSV1>0<T1>360<Yields><VGO>1</VGO><Distillates>0</Distillates><Naphtha>0</Naphtha><
Gases>0</Gases></Yields></T1><T2>370<Yields><VGO>1</VGO><Distillates>0</Distillates>
<Naphtha>0</Naphtha><Gases>0</Gases></Yields></T2><T3>380<Yields><VGO>1</VGO><Distil
lates>0</Distillates><Naphtha>0</Naphtha><Gases>0</Gases></Yields></T3><T4>390<Yield
s><VGO>1</VGO><Distillates>0</Distillates><Naphtha>0</Naphtha><Gases>0</Gases></Yiel
ds></T4></LHSV1>

<LHSV2>0.9523<T1>360<Yields><VGO>0.7324</VGO><Distillates>0.1866</Distillates><Naphth
a>0.0558</Naphtha><Gases>0.0117</Gases></Yields></T1><T2>370<Yields><VGO>0.7063</VG
O><Distillates>0.1993</Distillates><Naphtha>0.0682</Naphtha><Gases>0.013</Gases></Yi
elds></T2><T3>380<Yields><VGO>0.6755</VGO><Distillates>0.2139</Distillates><Naphtha>
0.0823</Naphtha><Gases>0.0164</Gases></Yields></T3><T4>390<Yields><VGO>0.6208</VGO><
Distillates>0.2456</Distillates><Naphtha>0.1028</Naphtha><Gases>0.0199</Gases></Yiel
ds></T4></LHSV2>

<LHSV3>1.111<T1>360<Yields><VGO>0.7147</VGO><Distillates>0.1984</Distillates><Naphth
a>0.0596</Naphtha><Gases>0.0137</Gases></Yields></T1><T2>370<Yields><VGO>0.6833</VG
O><Distillates>0.2091</Distillates><Naphtha>0.0791</Naphtha><Gases>0.0161</Gases></Yi
elds></T2><T3>380<Yields><VGO>0.6422</VGO><Distillates>0.2296</Distillates><Naphtha>
0.0956</Naphtha><Gases>0.0223</Gases></Yields></T3><T4>390<Yields><VGO>0.5655</VGO><
Distillates>0.2765</Distillates><Naphtha>0.1217</Naphtha><Gases>0.0286</Gases></Yiel
ds></T4></LHSV3>

<LHSV4>1.25<T1>360<Yields><VGO>0.6753</VGO><Distillates>0.2233</Distillates><Naphtha
>0.0713</Naphtha><Gases>0.0171</Gases></Yields></T1><T2>370<Yields><VGO>0.6312</VGO>
<Distillates>0.2441</Distillates><Naphtha>0.0892</Naphtha><Gases>0.0254</Gases></Yie

```

```

lds></T2><T3>380<Yields><VGO>0.5767</VGO><Distillates>0.2677</Distillates><Naphtha>0
.1196</Naphtha><Gases>0.0281</Gases></Yields></T3><T4>390<Yields><VGO>0.5094</VGO><D
istillates>0.3155</Distillates><Naphtha>0.1393</Naphtha><Gases>0.0323</Gases></Yield
s></T4></LHSV4>
</Operationconditions>
</VR4>
</Validationresults>
</Hydrocracking>
<Therm_Cracking>
<Mechanism1>
<Name>Jacob</Name>
<Lumps>10</Lumps>
<Year>1976</Year>
<speciesData id="species_data">
  <species1 name="Ph">
    <density units="kg/m3">900</density>
    <PesoM units="kg/kmol">400</PesoM>
  </species1>
  <species2 name="Nh">
    <density units="kg/m3">850</density>
    <PesoM units="kg/kmol">400</PesoM>
  </species2>
  <species3 name="Ah">
    <density units="kg/m3">875</density>
    <PesoM units="kg/kmol">400</PesoM>
  </species3>
  <species4 name="Cah">
    <density units="kg/m3">880</density>
    <PesoM units="kg/kmol">400</PesoM>
  </species4>
  <species5 name="P1">
    <density units="kg/m3">750</density>
    <PesoM units="kg/kmol">200</PesoM>
  </species5>
  <species6 name="N1">
    <density units="kg/m3">775</density>
    <PesoM units="kg/kmol">200</PesoM>
  </species6>
  <species7 name="A1">
    <density units="kg/m3">780</density>
    <PesoM units="kg/kmol">200</PesoM>
  </species7>
  <species8 name="Ca1">
    <density units="kg/m3">715</density>
    <PesoM units="kg/kmol">200</PesoM>
  </species8>
  <species9 name="Gas">
    <density units="kg/m3">100</density>
    <PesoM units="kg/kmol">50</PesoM>
  </species9>
  <species10 name="coque">
    <density units="kg/m3">1800</density>
    <PesoM units="kg/kmol">12</PesoM>
  </species10>
</speciesData>
<reactionData id="reaction_data">
  <reaction id="01" Reversible="No">
    <Equation>Ph--&gt;P1</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.196<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ph</Reactants>
    <Products>P1</Products>
  </reaction>
  <reaction id="02" Reversible="No">
    <Equation>Nh--&gt;N1</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.196<!--at 1000°F--></Rate>

```

```

    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>Nl</Products>
</reaction>
<reaction id="03" Reversible="No">
  <Equation>Ah--&gt;Al</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.196<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>Al</Products>
</reaction>
<reaction id="04" Reversible="No">
  <Equation>Ah--&gt;Rl</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.489<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>Rl</Products>
</reaction>
<reaction id="05" Reversible="No">
  <Equation>Rh--&gt;Rl</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.049<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Rh</Reactants>
  <Products>Rl</Products>
</reaction>
<reaction id="06" Reversible="No">
  <Equation>Ph--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.611<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ph</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="07" Reversible="No">
  <Equation>Nh--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">9900</ActEner>
    <Rate units="1/s">0.939<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Nh</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="08" Reversible="No">
  <Equation>Ah--&gt;G</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">26100</ActEner>
    <Rate units="1/s">0.685<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>Ah</Reactants>
  <Products>G</Products>
</reaction>
<reaction id="09" Reversible="No">
  <Equation>Ph--&gt;coque</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">31500</ActEner>
    <Rate units="1/s">0.099<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>

```

```

</Ratecoeff>
<Reactants>Ph</Reactants>
<Products>coque</Products>
</reaction>
<reaction id="10" Reversible="No">
<Equation>Nh--&gt;Coque</Equation>
<Ratecoeff>
<ActEner units="Btu/lbmol">31500</ActEner>
<Rate units="1/s">0.149<!--at 1000°F--></Rate>
<HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>Nh</Reactants>
<Products>Coque</Products>
</reaction>
<reaction id="11" Reversible="No">
<Equation>Ah--&gt;coque</Equation>
<Ratecoeff>
<ActEner units="Btu/lbmol">31500</ActEner>
<Rate units="1/s">0.198<!--at 1000°F--></Rate>
<HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>Ah</Reactants>
<Products>coque</Products>
</reaction>
<reaction id="12" Reversible="No">
<Equation>Rh--&gt;coque</Equation>
<Ratecoeff>
<ActEner units="Btu/lbmol">31500</ActEner>
<Rate units="1/s">0.149<!--at 1000°F--></Rate>
<HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>Rh</Reactants>
<Products>coque</Products>
</reaction>
<reaction id="13" Reversible="No">
<Equation>P1--&gt;g</Equation>
<Ratecoeff>
<ActEner units="Btu/lbmol">9900</ActEner>
<Rate units="1/s">0.282<!--at 1000°F--></Rate>
<HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>P1</Reactants>
<Products>g</Products>
</reaction>
<reaction id="14" Reversible="No">
<Equation>N1--&gt;g</Equation>
<Ratecoeff>
<ActEner units="Btu/lbmol">9900</ActEner>
<Rate units="1/s">0.282<!--at 1000°F--></Rate>
<HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>N1</Reactants>
<Products>g</Products>
</reaction>
<reaction id="15" Reversible="No">
<Equation>A1--&gt;g</Equation>
<Ratecoeff>
<ActEner units="Btu/lbmol">26100</ActEner>
<Rate units="1/s">0.196<!--at 1000°F--></Rate>
<HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
</Ratecoeff>
<Reactants>A1</Reactants>
<Products>g</Products>
</reaction>
<reaction id="16" Reversible="No">
<Equation>P1--&gt;coque</Equation>
<Ratecoeff>
<ActEner units="Btu/lbmol">31500</ActEner>
<Rate units="1/s">0.099<!--at 1000°F--></Rate>
<HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
</Ratecoeff>

```

```

    <Reactants>P1</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="17" Reversible="No">
    <Equation>N1--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.099<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>N1</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="18" Reversible="No">
    <Equation>A1--&gt;c</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.050<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>A1</Reactants>
    <Products>c</Products>
  </reaction>
  <reaction id="19" Reversible="No">
    <Equation>R1--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.01<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>R1</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="20" Reversible="No">
    <Equation>g--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">18000</ActEner>
      <Rate units="1/s">0.048<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>g</Reactants>
    <Products>coque</Products>
  </reaction>
</reactionData>
</Mechanism1>
<Mechanism2>
  <Name>Weekman</Name>
  <Lumps>3</Lumps>
  <Year>1970</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Gas+coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>GO--&gt;Gasoline</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.1942</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gasoline</Products>
    </reaction>
  </reactionData>
</Mechanism2>

```

```

</reaction>
<reaction id="2" Reversible="No">
  <Equation>Gasoline--&gt;Gas+coke</Equation>
  <Ratecoeff>
    <velcons units="s^-1">0.0093</velcons>
  </Ratecoeff>
  <Reactants>Gasoline</Reactants>
  <Products>Gas+coke</Products>
</reaction>
<reaction id="3" Reversible="No">
  <Equation>GO--&gt;gas+coke</Equation>
  <Ratecoeff>
    <velcons units="wtfrac^-1 s^-1">0.0488</velcons>
  </Ratecoeff>
  <Reactants>GO</Reactants>
  <Products>gas+coke</Products>
</reaction>
</reactionData>
</Mechanism2>
<Mechanism3>
  <Name>Lee</Name>
  <Lumps>4</Lumps>
  <Year>1989</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>GO--&gt;Gasoline</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.1942</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gasoline</Products>
    </reaction>
    <reaction id="2" Reversible="No">
      <Equation>GO--&gt;Gas</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.0348</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gas</Products>
    </reaction>
    <reaction id="3" Reversible="No">
      <Equation>GO--&gt;coke</Equation>
      <Ratecoeff>
        <velcons units="wtfrac^-1 s^-1">0.0140</velcons>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>coke</Products>
    </reaction>
    <reaction id="4" Reversible="No">
      <Equation>Gne--&gt;Gas</Equation>
      <Ratecoeff>
        <velcons units=" s^-1">0.0093</velcons>
      </Ratecoeff>

```

```

    <Reactants>Gne</Reactants>
    <Products>Gas</Products>
  </reaction>
  <reaction id="5" Reversible="No">
    <Equation>Gne--Coke</Equation>
    <Ratecoeff>
      <velcons units="s^-1">0.00000002</velcons>
    </Ratecoeff>
    <Reactants>Gne</Reactants>
    <Products>Coke</Products>
  </reaction>
</reactionData>
</Mechanism3>
<Mechanism4>
  <Name>Larocca</Name>
  <Lumps>5</Lumps>
  <Year>1990</Year>
  <speciesData id="species_data">
    <species1 name="SVG0">
      <sgravity units="-o-">0.9389</sgravity>
      <TBP units="K">
        <IBP>534</IBP>
        <wt5>573</wt5>
        <wt10>595</wt10>
        <wt30>630</wt30>
        <wt50>660</wt50>
        <wt70>696</wt70>
        <wt90>747</wt90>
        <wt95>771</wt95>
        <FBP>817</FBP>
      </TBP>
    </species1>
    <species2 name="ParafinicVGO">
      <sgravity units="-o-">0.9039</sgravity>
      <TBP units="K">
        <IBP>482</IBP>
        <wt5>537</wt5>
        <wt10>558</wt10>
        <wt30>609</wt30>
        <wt50>648</wt50>
        <wt70>691</wt70>
        <wt90>743</wt90>
        <wt95>765</wt95>
        <FBP>817</FBP>
      </TBP>
    </species2>
    <species3 name="P">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="N">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
    <species5 name="A">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species5>
    <species6 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species6>
    <species7 name="gas+coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species7>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>P--&gt; gas+coke</Equation>
      <Ratecoeff>

```

```

    <velcons units="cm^3 gcat^-1 s^-1">6.6</velcons>
  </Ratecoeff>
  <Reactants>P</Reactants>
  <Products>gas+coke</Products>
</reaction>
<reaction id="2" Reversible="No">
  <Equation>P--&gt;Gne</Equation>
  <Ratecoeff>
    <velcons units="cm^3 gcat^-1 s^-1">6.6</velcons>
  </Ratecoeff>
  <Reactants>P</Reactants>
  <Products>Gne</Products>
</reaction>
<reaction id="3" Reversible="No">
  <Equation>N--&gt;gas+coke</Equation>
  <Ratecoeff>
    <velcons units="cm^3 gcat^-1 s^-1">1.4</velcons>
  </Ratecoeff>
  <Reactants>N</Reactants>
  <Products>gas+coke</Products>
</reaction>
<reaction id="4" Reversible="No">
  <Equation>N--&gt;Gne</Equation>
  <Ratecoeff>
    <velcons units="cm^3 gcat^-1 s^-1">7.1</velcons>
  </Ratecoeff>
  <Reactants>N</Reactants>
  <Products>Gne</Products>
</reaction>
<reaction id="5" Reversible="No">
  <Equation>A--&gt;gas+coke</Equation>
  <Ratecoeff>
    <velcons units="cm^3 gcat^-1 s^-1">1.1</velcons>
  </Ratecoeff>
  <Reactants>A</Reactants>
  <Products>gas+coke</Products>
</reaction>
<reaction id="6" Reversible="No">
  <Equation>A--&gt;Gne</Equation>
  <Ratecoeff>
    <velcons units="cm^3 gcat^-1 s^-1">17.1</velcons>
  </Ratecoeff>
  <Reactants>A</Reactants>
  <Products>Gne</Products>
</reaction>
</reactionData>
</Mechanism4>
<Mechanism5>
  <Name>Ancheyta</Name>
  <Lumps>5</Lumps>
  <Year>1997</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <API units="">25.5</API>
      <TBP units="k">
        <IBP>508</IBP>
        <wt30>682</wt30>
        <wt50>706</wt50>
        <wt70>740</wt70>
        <wt90>790</wt90>
        <FBP>841</FBP>
      </TBP>
      <sgravity units="-o-">0.9013</sgravity>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Dry Gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
  </speciesData>

```



```

</species3>
<species4 name="coke">
  <density units="kg/m3">-0</density>
  <PesoM units="kg/kmol">-0</PesoM>
</species4>
<species5 name="LPG">
  <density units="kg/m3">-0</density>
  <PesoM units="kg/kmol">-0</PesoM>
</species5>
</speciesData>
<reactionData id="reaction_data">
  <reaction id="1" Reversible="No">
    <Equation>GO--&gt;Gasoline</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.1942</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>Gasoline</Products>
  </reaction>
  <reaction id="2" Reversible="No">
    <Equation>GO--&gt;LPG</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0357</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>LPG</Products>
  </reaction>
  <reaction id="3" Reversible="No">
    <Equation>GO--&gt;DG</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0001</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>DG</Products>
  </reaction>
  <reaction id="4" Reversible="No">
    <Equation>GO--&gt;coke</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0140</velcons>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>coke</Products>
  </reaction>
  <reaction id="5" Reversible="No">
    <Equation>Gne--&gt;LPG</Equation>
    <Ratecoeff>
      <velcons units="s^-1">0.0061</velcons>
    </Ratecoeff>
    <Reactants>Gne</Reactants>
    <Products>LPG</Products>
  </reaction>
  <reaction id="6" Reversible="No">
    <Equation>Gne--&gt;DG</Equation>
    <Ratecoeff>
      <velcons units="s^-1">0.0032</velcons>
    </Ratecoeff>
    <Reactants>Gne</Reactants>
    <Products>DG</Products>
  </reaction>
  <reaction id="7" Reversible="No">
    <Equation>Gne--&gt;coke</Equation>
    <Ratecoeff>
      <velcons units="s^-1">0.00000002</velcons>
    </Ratecoeff>
    <Reactants>Gne</Reactants>
    <Products>coke</Products>
  </reaction>
  <reaction id="8" Reversible="No">
    <Equation>LPG--&gt;DG</Equation>
    <Ratecoeff>
      <velcons units="s^-1">0.0020</velcons>

```

```

    </Ratecoeff>
    <Reactants>LPG</Reactants>
    <Products>DG</Products>
  </reaction>
</reactionData>
</Mechanism5>
<Mechanism6>
  <Name>Hagelberg</Name>
  <Lumps>8</Lumps>
  <Year>2002</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species1>
    <species2 name="Gparafins">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="Golefins">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="Gnaphthenes">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
    <species5 name="Garomatics">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species5>
    <species6 name="LPG">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species6>
    <species name="Dry Gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species>
    <species8 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species8>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>GO--&gt;Gparafins</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.024</velcons>
        <ActEner units="kJ/mol">75</ActEner>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gparafins</Products>
    </reaction>
    <reaction id="2" Reversible="No">
      <Equation>GO--&gt;Golefins</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.044</velcons>
        <ActEner units="kJ/mol">106</ActEner>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Golefins</Products>
    </reaction>
    <reaction id="3" Reversible="No">
      <Equation>GO--&gt;Gnaphthenes</Equation>
      <Ratecoeff>
        <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.009</velcons>
        <ActEner units="kJ/mol">68</ActEner>
      </Ratecoeff>
      <Reactants>GO</Reactants>
      <Products>Gnaphthenes</Products>
    </reaction>
  </reactionData>
</Mechanism6>

```

```

</reaction>
<reaction id="4" Reversible="No">
  <Equation>GO--&gt;Garomatics</Equation>
  <Ratecoeff>
    <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.028</velcons>
    <ActEner units="kJ/mol">95</ActEner>
  </Ratecoeff>
  <Reactants>GO</Reactants>
  <Products>Garomatics</Products>
</reaction>
<reaction id="5" Reversible="No">
  <Equation>Golefins--&gt;LPG</Equation>
  <Ratecoeff>
    <velcons units="s^-1">0.27</velcons>
    <ActEner units="kJ/mol">98</ActEner>
  </Ratecoeff>
  <Reactants>Golefins</Reactants>
  <Products>LPG</Products>
</reaction>
<reaction id="6" Reversible="No">
  <Equation>GO--&gt;coke</Equation>
  <Ratecoeff>
    <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.013</velcons>
    <ActEner units="kJ/mol">66</ActEner>
  </Ratecoeff>
  <Reactants>GO</Reactants>
  <Products>coke</Products>
</reaction>
<reaction id="7" Reversible="No">
  <Equation>GO--&gt;Dry Gas</Equation>
  <Ratecoeff>
    <velcons units=" s^-1">3.0</velcons>
    <ActEner units="kJ/mol">190</ActEner>
  </Ratecoeff>
  <Reactants>GO</Reactants>
  <Products>Dry Gas</Products>
</reaction>
<reaction id="8" Reversible="No">
  <Equation>GO--&gt;LPG</Equation>
  <Ratecoeff>
    <velcons units="m^6 mol^-1 kgcat^-1 s^-1">0.020</velcons>
    <ActEner units="kJ/mol">88</ActEner>
  </Ratecoeff>
  <Reactants>GO</Reactants>
  <Products>LPG</Products>
</reaction>
</reactionData>
</Mechanism6>
<Mechanism7>
  <Name>Bollas</Name>
  <Lumps>5</Lumps>
  <Year>2007</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <API units="">25.2</API>
      <TBP units="k">
        <IBP>539.3</IBP>
        <wt10>591.6</wt10>
        <wt30>658.5</wt30>
        <wt50>698.4</wt50>
        <wt70>726</wt70>
        <wt90>758.4</wt90>
        <FBP>782.4</FBP>
      </TBP>
      <sgravity units="-o-">0.903</sgravity>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0-</density>
      <PesoM units="kg/kmol">-0-</PesoM>
    </species2>
    <species3 name="Dry Gas">

```

```

    <density units="kg/m3">-0-</density>
    <PesoM units="kg/kmol">-0-</PesoM>
  </species3>
  <species4 name="coke">
    <density units="kg/m3">-0-</density>
    <PesoM units="kg/kmol">-0-</PesoM>
  </species4>
  <species5 name="LPG">
    <density units="kg/m3">-0-</density>
    <PesoM units="kg/kmol">-0-</PesoM>
  </species5>
</speciesData>
<reactionData id="reaction_data">
  <reaction id="1" Reversible="No">
    <Equation>GO--&gt;Gasoline</Equation>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.021</velcons>
      <ActEner units="kcal/gmol">7.46</ActEner>
      <Rate units="wtfrac^-1 s^-1">0.07<!--at 520°C--></Rate>
    </Ratecoeff>
    <Reactants>GO</Reactants>
    <Products>Gasoline</Products>
  </reaction>
  <reaction id="2" Reversible="No">
    <Equation>GO--&gt;LPG</Equation>
    <Reactants>GO</Reactants>
    <Products>LPG</Products>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0057</velcons>
      <ActEner units="kcal/gmol">10.29</ActEner>
      <Rate units="wtfrac^-1 s^-1">0.11<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="3" Reversible="No">
    <Equation>GO--&gt;DG</Equation>
    <Reactants>GO</Reactants>
    <Products>DG</Products>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.0013</velcons>
      <ActEner units="kcal/gmol">17.70</ActEner>
      <Rate units="wtfrac^-1 s^-1">2.83<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="4" Reversible="No">
    <Equation>GO--&gt;coke</Equation>
    <Reactants>GO</Reactants>
    <Products>coke</Products>
    <Ratecoeff>
      <velcons units="wtfrac^-1 s^-1">0.007913</velcons>
      <ActEner units="kcal/gmol">2.87</ActEner>
      <Rate units="wtfrac^-1 s^-1">0.00014<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="5" Reversible="No">
    <Equation>Gne--&gt;LPG</Equation>
    <Reactants>Gne</Reactants>
    <Products>LPG</Products>
    <Ratecoeff>
      <velcons units=" s^-1">0.00085</velcons>
      <ActEner units="kcal/gmol">16.11</ActEner>
      <Rate units="1/s">22.82<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="6" Reversible="No">
    <Equation>Gne--&gt;DG</Equation>
    <Reactants>Gne</Reactants>
    <Products>DG</Products>
    <Ratecoeff>
      <velcons units="s^-1">0.000014</velcons>
      <ActEner units="kcal/gmol">26.77</ActEner>
      <Rate units="1/s">31.41<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>

```

```

    </Ratecoeff>
  </reaction>
  <reaction id="7" Reversible="No">
    <Equation>Gne--&gt; coke</Equation>
    <Reactants>Gne</Reactants>
    <Products>coke</Products>
    <Ratecoeff>
      <velcons units="s^-1">0.00077</velcons>
      <ActEner units="kcal/gmol">3.33</ActEner>
      <Rate units="1/s">0.00632<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
  <reaction id="8" Reversible="No">
    <Equation>LPG--&gt; coke</Equation>
    <Reactants>LPG</Reactants>
    <Products>coke</Products>
    <Ratecoeff>
      <velcons units="s^-1">0.00001</velcons>
      <ActEner units="kcal/gmol">23.60</ActEner>
      <Rate units="1/s">31.82<!--at 520°C--></Rate>
    </Ratecoeff>
  </reaction>
</reactionData>
</Mechanism7>
<Mechanism8>
  <Name>Barbosa</Name>
  <Lumps>11</Lumps>
  <Year>2013</Year>
  <speciesData id="species_data">
    <species1 name="Ph">
      <density units="kg/m3">900</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species1>
    <species2 name="Nh">
      <density units="kg/m3">850</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species2>
    <species3 name="Ah">
      <density units="kg/m3">875</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species3>
    <species4 name="Cah">
      <density units="kg/m3">880</density>
      <PesoM units="kg/kmol">400</PesoM>
    </species4>
    <species5 name="P1">
      <density units="kg/m3">750</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species5>
    <species6 name="N1">
      <density units="kg/m3">775</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species6>
    <species7 name="A1">
      <density units="kg/m3">780</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species7>
    <species8 name="Ca1">
      <density units="kg/m3">715</density>
      <PesoM units="kg/kmol">200</PesoM>
    </species8>
    <species9 name="Gas">
      <density units="kg/m3">100</density>
      <PesoM units="kg/kmol">50</PesoM>
    </species9>
    <species10 name="coque">
      <density units="kg/m3">1800</density>
      <PesoM units="kg/kmol">12</PesoM>
    </species10>
    <species11 name="Dry Gas">
      <density units="kg/m3">155</density>

```

```

    <PesoM units="kg/kmol">18.4</PesoM>
  </species11>
</speciesData>
<reactionData id="reaction_data">
  <reaction id="01" Reversible="No">
    <Equation>Ph--&gt;P1</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.196<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ph</Reactants>
    <Products>P1</Products>
  </reaction>
  <reaction id="02" Reversible="No">
    <Equation>Nh--&gt;N1</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.196<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Nh</Reactants>
    <Products>N1</Products>
  </reaction>
  <reaction id="03" Reversible="No">
    <Equation>Ah--&gt;A1</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.196<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>A1</Products>
  </reaction>
  <reaction id="04" Reversible="No">
    <Equation>Ah--&gt;R1</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.489<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>R1</Products>
  </reaction>
  <reaction id="05" Reversible="No">
    <Equation>Rh--&gt;R1</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.049<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">25<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Rh</Reactants>
    <Products>R1</Products>
  </reaction>
  <reaction id="06" Reversible="No">
    <Equation>Ph--&gt;G</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">9900</ActEner>
      <Rate units="1/s">0.611<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ph</Reactants>
    <Products>G</Products>
  </reaction>
  <reaction id="07" Reversible="No">
    <Equation>Nh--&gt;G</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">9900</ActEner>
      <Rate units="1/s">0.939<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
    </Ratecoeff>

```

```

    <Reactants>Nh</Reactants>
    <Products>G</Products>
  </reaction>
  <reaction id="08" Reversible="No">
    <Equation>Ah--&gt;G</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.685<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">65<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>G</Products>
  </reaction>
  <reaction id="09" Reversible="No">
    <Equation>Ph--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.099<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ph</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="10" Reversible="No">
    <Equation>Nh--&gt;Coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.149<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Nh</Reactants>
    <Products>Coque</Products>
  </reaction>
  <reaction id="11" Reversible="No">
    <Equation>Ah--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.198<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Ah</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="12" Reversible="No">
    <Equation>Rh--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.149<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">225<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Rh</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="13" Reversible="No">
    <Equation>P1--&gt;g</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">9900</ActEner>
      <Rate units="1/s">0.282<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>P1</Reactants>
    <Products>g</Products>
  </reaction>
  <reaction id="14" Reversible="No">
    <Equation>N1--&gt;g</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">9900</ActEner>
      <Rate units="1/s">0.282<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>N1</Reactants>

```

```

    <Products>g</Products>
  </reaction>
  <reaction id="15" Reversible="No">
    <Equation>Al--&gt;g</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">26100</ActEner>
      <Rate units="1/s">0.196<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">40<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Al</Reactants>
    <Products>g</Products>
  </reaction>
  <reaction id="16" Reversible="No">
    <Equation>P1--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.099<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>P1</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="17" Reversible="No">
    <Equation>N1--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.099<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>N1</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="18" Reversible="No">
    <Equation>Al--&gt;c</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.050<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>Al</Reactants>
    <Products>c</Products>
  </reaction>
  <reaction id="19" Reversible="No">
    <Equation>R1--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">31500</ActEner>
      <Rate units="1/s">0.01<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">200<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>R1</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="20" Reversible="No">
    <Equation>g--&gt;coque</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">18000</ActEner>
      <Rate units="1/s">0.048<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>g</Reactants>
    <Products>coque</Products>
  </reaction>
  <reaction id="21" Reversible="No">
    <Equation>HFO--&gt;DG</Equation>
    <Ratecoeff>
      <ActEner units="Btu/lbmol">18000</ActEner>
      <Rate units="1/s">0.048<!--at 1000°F--></Rate>
      <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
    </Ratecoeff>
    <Reactants>HFO</Reactants>
    <Products>DG</Products>
  </reaction>

```



```

</reaction>
<reaction id="22" Reversible="No">
  <Equation>LFO--&gt;DG</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">0.282</ActEner>
    <Rate units="1/s">0.060<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>LFO</Reactants>
  <Products>DG</Products>
</reaction>
<reaction id="23" Reversible="No">
  <Equation>g--&gt;DG</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">0.048</ActEner>
    <Rate units="1/s">0.042<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>g</Reactants>
  <Products>DG</Products>
</reaction>
<reaction id="24" Reversible="No">
  <Equation>coque--&gt;DG</Equation>
  <Ratecoeff>
    <ActEner units="Btu/lbmol">0.048</ActEner>
    <Rate units="1/s">0.042<!--at 1000°F--></Rate>
    <HOR units="Btu/lb">160<!--Heat of reaction--></HOR>
  </Ratecoeff>
  <Reactants>coque</Reactants>
  <Products>DG</Products>
</reaction>
</reactionData>
</Mechanism8>
<Mechanism9>
  <Name>Gianetto</Name>
  <Lumps>3</Lumps>
  <Year>1994</Year>
  <speciesData id="species_data">
    <species1 name="VGO">
      <TBP units="k">
        <IBP>539.45</IBP>
        <wt5>573.15</wt5>
        <wt10>595</wt10>
        <wt30>630</wt30>
        <wt50>660</wt50>
        <wt70>696</wt70>
        <wt90>747</wt90>
        <wt95>771</wt95>
        <FBP>817</FBP>
      </TBP>
      <sgravity units="-o-">0.9389</sgravity>
    </species1>
    <species2 name="Gasoline">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species2>
    <species3 name="light gas">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species3>
    <species4 name="coke">
      <density units="kg/m3">-0</density>
      <PesoM units="kg/kmol">-0</PesoM>
    </species4>
  </speciesData>
  <reactionData id="reaction_data">
    <reaction id="1" Reversible="No">
      <Equation>VGO--&gt;light gases</Equation>
      <Ratecoeff>
        <velcons units="m^6 kmol^-1 kgcat^-1 s^-1">941900000000</velcons>
        <ActEner units="cal/mol">22795.3</ActEner>
      </Ratecoeff>
    </reaction>
  </reactionData>

```

```
</Ratecoeff>
<Reactants>VGO</Reactants>
<Products>light gases</Products>
</reaction>
<reaction id="2" Reversible="No">
  <Equation>VGO--&gt;Gasoline</Equation>
  <Ratecoeff>
    <velcons units="m^6 kmol^-1 kgcat^-1 s^-1">376900000000000</velcons>
    <ActEner units="cal/mol">29900.5</ActEner>
  </Ratecoeff>
  <Reactants>VGO</Reactants>
  <Products>Gasoline</Products>
</reaction>
<reaction id="3" Reversible="No">
  <Equation>VGO--&gt;coke</Equation>
  <Ratecoeff>
    <velcons units="m^6 mol^-1 kgcat^-1 s^-1">107000000000000</velcons>
    <ActEner units="cal/mol">34824</ActEner>
  </Ratecoeff>
  <Reactants>VGO</Reactants>
  <Products>coke</Products>
</reaction>
<reaction id="4" Reversible="No">
  <Equation>Gasoline--&gt;gas+coke</Equation>
  <Ratecoeff>
    <velcons units="m^3 kgcat^-1 s^-1">1093</velcons>
    <ActEner units="cal/mol">11402.3</ActEner>
  </Ratecoeff>
  <Reactants>Gasoline</Reactants>
  <Products>gas+coke</Products>
</reaction>
</reactionData>
</Mechanism9>
</Therm_Cracking>
</Mechanisms>
```

# References

- [1] S. M. Jacob, S. E. Voltz, and V. M. Weekman, "A Lumping and Reaction Scheme for Catalytic Cracking," *AIChE Journal*, vol. 22, no. 22, pp. 701–713, 1976.
- [2] A. C. Barbosa, G. C. Lopes, L. M. Rosa, and M. Mori, "Three Dimensional Simulation of Catalytic Cracking Reactions in an Industrial Scale Riser Using a 11-lump Kinetic," *Chemical Engineering Transactions*, vol. 32, pp. 637–642, 2013.
- [3] S. A. Qader and G. R. Hill, "Hydrocracking of Gas Oil," *Industrial & Engineering Chemistry Process Design and Development*, vol. 8, no. 1, pp. 98–105, 1969.
- [4] V. W. Weekman and D. M. Nace, "Kinetics of catalytic cracking selectivity in fixed, moving, and fluid bed reactors," *AIChE Journal*, vol. 16, pp. 397–404, May 1970.
- [5] A. Arbel, Z. Huang, I. H. Rinard, R. Shinnar, and A. V. Sapre, "Dynamic and Control of Fluidized Catalytic Crackers. 1. Modeling of the Current Generation of FCC's," *Industrial & Engineering Chemistry Research*, vol. 34, no. 4, pp. 1228–1243, 1995.
- [6] J. M. Arandes, I. Abajo, I. Fernandez, D. Lopez, and B. J., "Kinetics of Gaseous Product Formation in the Coke Combustion of a Fluidized Catalytic Cracking Catalyst," *Industrial Chemical Engineering*, no. 3, pp. 3255–3260, 1999.
- [7] J. M. Arandes, M. J. Azkoiti, J. Bilbao, and H. I. de Lasa, "Modelling fcc units under steady and unsteady state conditions," *The Canadian Journal of Chemical Engineering*, vol. 78, no. 1, pp. 111–123, 2000.
- [8] A. D. Bianco, N. Panariti, M. Anelli, P. L. Beltrame, and P. Carniti, "Thermal cracking of petroleum residues: 1. Kinetic analysis of the reaction," *Fuel*, vol. 72, no. 1, pp. 75–80, 1993.
- [9] A.N. Sawarkar, A. Pandit, and J. B. Joshi, "Studies in Coking of Arabian Mix Vacuum

- Residue,” *Chemical Engineering Research and Design*, vol. 85, pp. 481–491, Jan. 2007.
- [10] R. O. Koseoglu and C. R. Phillips, “Kinetic models for the non-catalytic hydrocracking of Athabasca bitumen,” *Fuel*, vol. 67, no. 7, pp. 906–915, 1988.
- [11] L. G. Mendonça-Filho, *Modelagem e Simulação de Reator Trifásico Aplicado a Óleos Pesados com Reações de Hidrocraqueamento Térmico e Catalítico, Demetalização Deposição de Coque na Mistura e no Catalisador*. PhD thesis, UNICAMP, Campinas-SP, Brazil, 1998.
- [12] J. Martínez and J. Ancheyta, “Kinetic model for hydrocracking of heavy oil in a CSTR involving short term catalyst deactivation,” *Fuel*, vol. 100, pp. 193–199, Oct. 2012.
- [13] K. Aboul-Gheit, “Hydrocracking of Vacuum Gas Oil (VGO) for Fuels Production- Reaction Kinetics,” *Erdol Erdgas Kohle*, vol. 105, no. 7-8, pp. 319–320, 1989.
- [14] S. Sadighi, A. Ahmad, and M. Rashidzadeh, “4-Lump kinetic model for vacuum gas oil hydrocracker involving hydrogen consumption,” *Korean Journal of Chemical Engineering*, vol. 27, pp. 1099–1108, June 2010.
- [15] C. Botchwey, A. K. Dalai, and J. Adjaye, “Kinetics of Bitumen-Derived Gas Oil Upgrading Using a Commercial NiMo/Al<sub>2</sub>O<sub>3</sub> Catalyst,” *The Canadian Journal of Chemical Engineering*, vol. 82, pp. 478–487, 2004.
- [16] M. Ali, T. Tatsumi, and T. Masuda, “Development of heavy oil hydrocracking catalysts using amorphous silica-alumina and zeolites as catalyst supports,” *Applied Catalysis A: General*, vol. 233, no. 1 - 2, pp. 77 – 90, 2002.
- [17] S. Mohanty, D. N. Saraf, and D. Kunzru, “Modeling of a hydrocracking reactor,” *Fuel Processing Technology*, vol. 29, no. 1, pp. 1–17, 1991.
- [18] H. Ali, S. Rohani, and J. P. Corriou, “Modelling and Control of a Riser Type Fluid Catalytic Cracking (FCC) Unit,” *Chemical Engineering Research and Design*, vol. 75, no. 4, pp. 401–412, 1997.
- [19] P. K. Dasila, I. Choudhury, D. Saraf, S. Chopra, and A. Dalai, “Parametric Sensitivity Studies in a Commercial FCC Unit,” *Advances in Chemical Engineering and Science*, vol. 2, no. 1, pp. 136–149, 2012.
- [20] G. C. Lopes, L. M. Rosa, M. Mori, J. R. Nunhez, and W. P. Martignoni, “Three-

- dimensional modeling of fluid catalytic cracking industrial riser flow and reactions,” *Computers & Chemical Engineering*, vol. 35, pp. 2159–2168, Nov. 2011.
- [21] P. K. Dasila, I. R. Choudhury, S. Singh, S. Rajagopal, S. J. Chopra, and D. N. Sarraf, “Simulation of an Industrial Fluid Catalytic Cracking Riser Reactor Using a Novel 10-Lump Kinetic Model and Some Parametric Sensitivity Studies,” *Industrial & Engineering Chemistry Research*, vol. 53, no. 51, pp. 19660–19670, 2014.
- [22] J. Chang, K. Zhang, F. Meng, L. Wang, and X. Wei, “Computational investigation of hydrodynamics and cracking reaction in a heavy oil riser reactor,” *Particuology*, vol. 10, pp. 184–195, Apr. 2012.
- [23] J. Chang, W. Cai, K. Zhang, F. Meng, L. Wang, and Y. Yang, “Computational investigation of the hydrodynamics, heat transfer and kinetic reaction in an FCC gasoline riser,” *Chemical Engineering Science*, vol. 111, pp. 170–179, May 2014.
- [24] E. Baudrez, G. J. Heynderickx, and G. B. Marin, “Steady-state simulation of Fluid Catalytic Cracking riser reactors using a decoupled solution method with feedback of the cracking reactions on the flow,” *Chemical Engineering Research and Design*, vol. 88, pp. 290–303, Mar. 2010.
- [25] A. Gianetto, H. I. Farag, A. P. Blasetti, and H. I. de Lasa, “Fluid Catalytic Cracking Catalyst for Reformulated Gasolines. Kinetic Modeling,” *Industrial & Engineering Chemistry Research*, vol. 33, no. 12, pp. 3053–3062, 1994.
- [26] M. Ahsan, “Prediction of gasoline yield in a fluid catalytic cracking (FCC) riser using epsilon turbulence and 4-lump kinetic models: A computational fluid dynamics (CFD) approach,” *Journal of King Saud University - Engineering Sciences*, vol. 27, no. 2, pp. 130–136, 2015.
- [27] X.-L. Zhou, S.-Z. Chen, and C.-L. Li, “A Predictive Kinetic Model for Delayed Coking,” *Petroleum Science and Technology*, vol. 25, pp. 1539–1548, Dec. 2007.
- [28] D. I. Orochko, I. Perezhigina, S. P. Rogov, M. V. Rysakov, and G. N. Chernakova, “Applied over-all kinetics of hydrocracking of heavy petroleum distillates,” *Chemistry and Technology of Fuels and Oils*, vol. 8, no. 8, pp. 561–565, 1970.
- [29] S. M. Yui and E. C. Sandford, “Mild Hydrocracking of Bitumen-Derived Coker and Hydrocracker Heavy Gas Oils: Kinetics, Product Yields, and Product Properties,” *In-*

- dustrial and Engineering Chemistry*, vol. 28, pp. 1278–1284, 1989.
- [30] M. A. Callejas and M. T. Martinez, “Hydrocracking of a maya residue. kinetics and product yield distributions,” *Industrial & Engineering Chemistry Research*, vol. 38, no. 9, pp. 3285–3289, 1999.
- [31] K. Aoyagi, W. C. McCaffrey, and M. R. Gray, “Kinetics of Hydrocracking and Hydro-treating of Coker and Oilsands Gas Oils,” *Petroleum Science and Technology*, vol. 21, pp. 997–1015, Jan. 2003.
- [32] C. Botchwey, A. K. Dalai, and J. Adjaye, “Product Selectivity during Hydrotreating and Mild Hydrocracking of Bitumen-Derived Gas Oil,” *Energy & Fuels*, vol. 17, pp. 1372–1381, Sept. 2003.
- [33] S. Sánchez, M. A. Rodríguez, and J. Ancheyta, “Kinetic Model for Moderate Hydro-cracking of Heavy Oils,” *Industrial & Engineering Chemistry Research*, vol. 44, no. 25, pp. 9409–9413, 2005.
- [34] G. Valavarasu, M. Bhaskar, B. Sairam, K. S. Balaraman, and K. Balu, “A four lump kinetic model for the simulation of the hydrocracking process,” *Petroleum Science and Technology*, vol. 23, no. 11-12, pp. 1323–1332, 2005.
- [35] S. D. S. Asaee, L. Vafajoo, and F. Khorasheh, “A new approach to estimate parameters of a lumped kinetic model for hydroconversion of heavy residue,” *Fuel*, vol. 134, pp. 343 – 353, 2014.
- [36] L.-S. Lee, Y.-W. Chen, T.-N. Huang, and W.-Y. Pan, “Four-lump kinetic model for fluid catalytic cracking process,” *The Canadian Journal of Chemical Engineering*, vol. 67, pp. 615–619, Aug. 1989.
- [37] K. N. Theologos and N. C. Markatos, “Advanced modeling of fluid catalytic cracking riser-type reactors,” *AIChE Journal*, vol. 39, no. 6, pp. 1007–1017, 1993.
- [38] K. N. Theologos, I. D. Nikou, A. I. Lygeros, and N. C. Markatos, “Simulation and design of Fluid Catalytic Cracking riser-type reactors,” *Computers & Chemical Engineering*, vol. 20, no. 0, pp. 757–762, 1996.
- [39] P. G. Coxson and K. B. Bischoff, “Lumping strategy. 1. Introductory techniques and applications of cluster analysis,” *Industrial & Engineering Chemistry Research*, vol. 26,

- no. 6, pp. 1239–1248, 1987.
- [40] J. Corella and E. Frances, “On the Kinetic Equation of Deactivation of Commercial Cracking (FCC) Catalysts with Commercial Feedstocks,” in *Catalyst Deactivation 1991 Proceedings of the 5th International Symposium*, vol. 68 of *Studies in Surface Science and Catalysis*, pp. 375–381, Elsevier, 1991.
- [41] M. Ahsan, “Computational fluid dynamics (CFD) prediction of mass fraction profiles of gas oil and gasoline in fluid catalytic cracking (FCC) riser,” *Ain Shams Engineering Journal*, vol. 3, no. 4, pp. 403–409, 2012.
- [42] M. Ahsan, “Prediction of gasoline yield in a fluid catalytic cracking (FCC) riser using k-epsilon turbulence and 4-lump kinetic models: A computational fluid dynamics (CFD) approach,” *Journal of King Saud University - Engineering Sciences*, pp. 1–7, Sept. 2013.
- [43] X. Lan, C. Xu, G. Wang, L. Wu, and J. Gao, “CFD modeling of gas and solid flow and cracking reaction in two-stage riser reactors,” *Chemical Engineering Science*, vol. 64, no. 17, pp. 3847–3858, 2009.
- [44] M. Larocca, S. Ng, and H. De Lasa, “Fast catalytic cracking of heavy gas oils: modeling coke deactivation,” *Industrial & Engineering Chemistry Research*, vol. 29, pp. 171–180, Feb. 1990.
- [45] J. Ancheyta-Juarez, F. Lopez-Isunza, E. Aguilar-Rodriguez, and J. C. Moreno-Mayorga, “A Strategy for Kinetic Parameter Estimation in the Fluid Catalytic Cracking Process,” *Industrial Chemical Engineering*, vol. 12, no. 36, pp. 5170–5174, 1997.
- [46] J. Ancheyta-Juarez, F. Lopez-Isunza, and E. Aguilar-Rodriguez, “5-Lump kinetic model for gas oil catalytic cracking,” *Applied Catalysis A: General*, vol. 177, no. 2, pp. 227–235, 1999.
- [47] P. Hagelberg, I. Eilos, J. Hiltunen, K. Lipiäinen, V. M. Niemi, J. Aittamaa, and a.O.I. Krause, “Kinetics of catalytic cracking with short contact times,” *Applied Catalysis A: General*, vol. 223, pp. 73–84, Jan. 2002.
- [48] I. Pitault, A. T. Bell, D. Nevicato, M. Forissier, and J.-R. Bernard, “Kinetic model based on a molecular description for catalytic cracking of vacuum gas oil,” *Chemical Engineering Science*, vol. 49, no. 24, pp. 4249–4262, 1994.

- [49] C. Derouin, D. Nevicato, M. Forissier, G. Wild, and J.-R. Bernard, "Hydrodynamics of Riser Units and Their Impact on FCC Operation," *Industrial & Engineering Chemistry Research*, vol. 36, no. 11, pp. 4504–4515, 1997.
- [50] R. K. Gupta, V. Kumar, and V. K. Srivastava, "A new generic approach for the modeling of fluid catalytic cracking (FCC) riser reactor," *Chemical Engineering Science*, vol. 62, pp. 4510–4528, Sept. 2007.
- [51] J. L. Fernandes, C. I. C. Pinheiro, N. M. C. Oliveira, A. I. Neto, and F. Ramoa-Ribeiro, "Steady state multiplicity in an UOP FCC unit with high-efficiency regenerator," *Chemical Engineering Science*, vol. 62, pp. 6308–6322, Nov. 2007.
- [52] J. L. Fernandes, J. J. Verstraete, C. I. C. Pinheiro, N. M. C. Oliveira, and F. Ramoa-Ribeiro, "Dynamic modelling of an industrial R2R FCC unit," *Chemical Engineering Science*, vol. 62, pp. 1184–1198, Feb. 2007.
- [53] J. L. Fernandes, C. I. C. Pinheiro, N. M. C. Oliveira, and F. Ramo, "Model Development and Validation of an Industrial UOP Fluid Catalytic Cracking Unit with a High-Efficiency Regenerator," *Industrial Engineering Chemical*, pp. 850–866, 2008.
- [54] G. Effects, A. F. Errazu, H. I. D. Lasa, and F. Sarti, "A fluidized bed catalytic cracking regenerator model," *The Canadian Journal of Chemical Engineering*, vol. 57, no. 2, pp. 191–197, 1979.
- [55] P. B. Weisz and R. B. Goodwin, "Combustion within of Carbonaceous Porous Catalyst Deposits Particles," *Journal of Catalysis*, vol. 227-236, pp. 227–236, 1966.
- [56] G. Bozzano and M. Dente, "A Mechanistic Approach to Delayed Coking Modelling," *European Symposium of the Working Party on Computer Aided Process Engineering*, pp. 529–534, 2005.
- [57] R. O. Koseoglu and C. R. Phillips, "Kinetics of non-catalytic hydrocracking of Athabasca bitumen," *Fuel*, vol. 66, no. 6, pp. 741–748, 1987.
- [58] J. G. Speight, "The Chemistry and Physics and Coking," *Chemical Engineering Research and Design*, vol. 15, no. 1, pp. 1–8, 1998.
- [59] I. A. Wiehe, "A phase separation kinetic model for coke formation," *Industrial Engineering Chemical Residue*, vol. 32, pp. 2447–2454, 1993.



- [60] B. Souza, E. M. Matos, R. Guirardello, and J. R. Nunhez, "Predicting coke formation due to thermal cracking inside tubes of petrochemical fired heaters using a fast CFD formulation," *Journal of Petroleum Science and Engineering*, vol. 51, pp. 138–148, Apr. 2006.
- [61] R. Radmanesh, E. Chan, and M. R. Gray, "Modeling of mass transfer and thermal cracking during the coking of Athabasca residues," *Chemical Engineering Science*, vol. 63, pp. 1683–1691, Mar. 2008.
- [62] K. L. Kataria, R. P. Kulkarni, A. B. Pandit, J. B. Joshi, and M. Kumar, "Kinetic Studies of Low Severity Visbreaking," *Industrial & Engineering Chemistry Research*, vol. 43, no. 6, pp. 1373–1387, 2004.
- [63] J. Singh, M. M. Kumar, A. K. Saxena, and S. Kumar, "Studies on thermal cracking behavior of residual feedstocks in a batch reactor," *Chemical Engineering Science*, vol. 59, pp. 4505–4515, Nov. 2004.
- [64] J. Singh, M. M. Kumar, A. K. Saxena, and S. Kumar, "Reaction pathways and product yields in mild thermal cracking of vacuum residues : A multi-lump kinetic model," vol. 108, pp. 239–248, 2005.
- [65] J. Singh, M. M. Kumar, A. K. Saxena, and S. Kumar, "Reaction pathways and product yields in mild thermal cracking of vacuum residues: A multi-lump kinetic model," *Chemical Engineering Journal*, vol. 108, pp. 239–248, Apr. 2005.
- [66] S. Ebrahimi, J. S. Moghaddas, and M. K. R. Aghjeh, "Study on thermal cracking behavior of petroleum residue," *Fuel*, vol. 87, pp. 1623–1627, July 2008.
- [67] J. Singh, S. Kumar, and M. O. Garg, "Kinetic modelling of thermal cracking of petroleum residues: A critique," *Fuel Processing Technology*, vol. 94, pp. 131–144, Feb. 2012.
- [68] F. Alhumaidan, A. Hauser, H. Al-rabiah, H. Lababidi, and R. Bouresli, "Studies on thermal cracking behavior of vacuum residues in Eureka process," vol. 109, pp. 635–646, 2013.
- [69] F. Alhumaidan, H. M. S. Lababidi, and H. Al-rabiah, "Thermal cracking kinetics of Kuwaiti vacuum residues in Eureka process," *Fuel*, vol. 103, pp. 923–931, 2013.

- [70] M. Syukri, B. Mohd, and B. Periyasamy, "Binary cracking kinetics for thermal cracking of vacuum residues in Eureka process," *Fuel*, vol. 134, pp. 618–627, 2014.
- [71] A. Braumann and M. Kraft, "Incorporating experimental uncertainties into multivariate granulation modelling," *Chemical Engineering Science*, vol. 65, no. 3, pp. 1088–1100, 2010.
- [72] S. Mosbach, A. Braumann, P. L. W. Man, C. A. Kastner, G. P. E. Brownbridge, and M. Kraft, "Iterative improvement of Bayesian parameter estimates for an engine model by means of experimental design," *Combustion and Flame*, vol. 159, no. 3, pp. 1303–1313, 2012.
- [73] A. Smallbone, A. Bhave, A. Braumann, M. Kraft, and A. Dris, "Moving Toward Establishing More Robust and Systematic Model Development for IC Engines Using Process Informatics," *SAE Technical Paper Series (2010-01-0152)*, 2010.
- [74] A. Brownbridge, GPE Smallbone, W. Phadungsukanan, S. Mosbach, M. Kraft, and B. Johansson, "Moving Toward Establishing More Robust and Systematic Model Development for IC Engines Using Process Informatics," *SAE Technical Paper Series (2011-01-0237)*, 2011.
- [75] L. A. Alcázar and J. Ancheyta, "Sensitivity analysis based methodology to estimate the best set of parameters for heterogeneous kinetic models," *Chemical Engineering Journal*, vol. 128, pp. 85–93, Apr. 2007.
- [76] B. Efron, "Bootstrap Methods: Another Look at the Jackknife," *Ann. Statist.*, vol. 7, no. 1, pp. 1–26, 1979.
- [77] D.-Q. Li, X.-S. Tang, and K.-K. Phoon, "Bootstrap method for characterizing the effect of uncertainty in shear strength parameters on slope reliability," *Reliability Engineering & System Safety*, vol. 140, pp. 99–106, 2015.
- [78] R. Agrawal, "The compensation effect: A fact or a fiction," *Journal of thermal analysis*, vol. 35, no. 3, pp. 909–917, 1989.
- [79] A. P. Dhupe, A. Gokarn, and L. Doraiswamy, "Investigations into the compensation effect at catalytic gasification of active charcoal by carbon dioxide," *Fuel*, vol. 70, no. 7, pp. 839 – 844, 1991.

- [80] T. W. Kwon, J. R. Kim, S. D. Kim, and W. H. Park, "Catalytic steam gasification of lignite char," *Fuel*, vol. 68, no. 4, pp. 416 – 421, 1989.
- [81] K. Yip, E. Ng, C.-Z. Li, J.-I. Hayashi, and H. Wu, "A mechanistic study on kinetic compensation effect during low-temperature oxidation of coal chars," *Proceedings of the Combustion Institute*, vol. 33, no. 2, pp. 1755 – 1762, 2011.
- [82] P. Garn, "An examination of the kinetic compensation effect," *Journal of thermal analysis*, vol. 7, no. 2, pp. 475–478, 1975.
- [83] L. Liu, , and Q.-X. Guo, "Isokinetic relationship, isoequilibrium relationship, and enthalpy entropy compensation," *Chemical Reviews*, vol. 101, no. 3, pp. 673–696, 2001. PMID: 11712500.
- [84] N. Koga and J. Sestak, "Kinetic compensation effect as a mathematical consequence of the exponential rate constant," *Thermochimica Acta*, vol. 182, no. 2, pp. 201 – 208, 1991.
- [85] J. Zsako, "The kinetic compensation effect," *Journal of thermal analysis*, vol. 9, no. 1, pp. 101–108, 1976.
- [86] G. C. Bond, M. A. Keane, H. Kral, and J. A. Lercher, "Compensation phenomena in heterogeneous catalysis: General principles and a possible explanation," *Catalysis Reviews*, vol. 42, no. 3, pp. 323–383, 2000.
- [87] A. Blasetti and H. de Lasa, "FCC Riser Unit Operated in the Heat Transfer Mode Kinetic Modeling," *Industrial & Engineering Chemistry Research*, vol. 36, no. 8, pp. 3223 – 3229, 1997.
- [88] "Grupo de Investigacion BIOFRUN. cited; Available from: <http://minas.medellin.unal.edu.co/gruposdeinvestigacion/biofrun/index.php/publications>," 2015.