COKE FORMATION DURING THERMAL CRACKING OF A HEAVY CRUDE OIL

Laura Cristina Urán Castaño

Universidad Nacional de Colombia, Sede Medellín
Facultad de Minas
Medellín, Colombia
2015
COKE FORMATION DURING THERMAL CRACKING OF A HEAVY CRUDE OIL

Laura Cristina Urán Castaño

Thesis presented as a partial requirement to obtain the degree of:

M.Sc. in Chemical Engineering

Advisor:
Alejandro Molina

Research group:
Bioprocessos y Flujos Reactivos

Universidad Nacional de Colombia, Sede Medellín
Facultad de Minas
Medellín, Colombia
2015
ABSTRACT

A pseudo-mechanism for the production of coke during the thermal cracking of a Colombian heavy crude oil was proposed based on thermal cracking experiments carried out at TGA and at horizontal tube furnace at atmospheric conditions. In-situ combustion (ISC) is a thermal method that improves the recovery of heavy crude oils and involves complex phenomena such as heat and mass transfers, low-temperature oxidation of the liquid phase (LTO), and cracking reactions that yield coke, a carbonaceous residue that, after high-temperature oxidation (HTO) produces the heat that reduces the oil viscosity increasing the recovery factor. During cracking experiments, Ottawa sand was mixed with crude oil, or with a mixture of maltenes and asphaltenes extracted from that oil, and placed under nitrogen atmosphere and heated at 2°C/min up to different reaction temperatures (300°C, 350°C, 400°C and 450°C) at atmospheric pressure conditions. Even tough atmospheric pressure conditions is not a realistic condition as oil reservoirs operate above atmospheric pressure, this study as part of a bigger project to study ISC it was the first that develop a setup and a methodolody able to study ISC reactions. After the first approximation that this study made, further work will be carried out to study ISC process at more realistic conditions. This study found that the main cracking products were volatiles that could be condensables and non-condensables and a solid residue. Proximate, elemental, GC-MS and SIMDIS analysis were performed to establish the composition of the cracking products, and to determine the advance in the cracking reactions. During cracking experiments each oil fraction yielded lower- and heavier-molecular weight products. e.g. maltenes yielded gas (mainly composed by methane CH₄), distillables (a condensable fraction with maximum 18 carbons), low-molecular-weight maltenes (LMWM, a condensable fraction with maximum 28 carbons, that results from the cracking of maltenes and asphaltenes), and asphaltenes. Whereas asphaltenes leaded to coke formation and to LMWM and gases. The proposed pseudo-mechanism considers the formation of lower- and heavier molecules, separates the evaporation process from the thermal cracking, and proposed new pseudo-components such as Maltenes* that represents the maltenes fraction after the evaporation process and the one available for thermal cracking, and LMWM that is an upgraded cracking product of the cracking of maltenes* and asphaltenes that had a yield of 0.28 g/gtot. Furthermore, the proposed
pseudo-mechanism proposes kinetic parameters for the thermal cracking of a Colombian heavy crude oil under in-situ combustion conditions at atmospheric pressure. The kinetic parameters were optimized by minimizing the sum of square error (SSE) between the experimental and calculated yields. A good coefficient of determination was obtained, \( R^2 = 0.97 \), using first order kinetic parameters. The physical interpretation of the value of kinetic parameters is complicated given the rather empirical approach used to find the kinetic parameters, it is important to note that most parameters in particular activation energies have values typical for chemical-controlled process, exceptions to this are the activation energies 26.4 and 9760 kJ/mol that are too low and too high that involve the decomposition of asphaltenes and are accompanied by very low pre-exponential factor. Future work may focus on reducing the empirical nature of this mechanism.

Keywords: In-situ combustion, thermal cracking, coke formation, kinetic pseudo-mechanism, low-molecular-weight maltenes (LMWM).
RESUMEN

Se propuso un pseudo-mecanismo para la formación de coque durante el craqueo térmico de un crudo pesado, este pseudo-mecanismo se basa en resultados de pruebas de craqueo térmico llevadas a cabo en TGA y horno horizontal usando como muestra un crudo pesado Colombiano. La combustión in situ (CIS) es un método térmico que mejora el factor de recobro de crudos pesados, envolviendo fenómenos complejos como la transferencia de calor y de masa, oxidación a baja temperatura de la fase líquida, reacciones de craqueo que terminan en la producción de coque, un residuo carbonoso que, después de una oxidación a alta temperatura produce el calor necesario para reducir la viscosidad del crudo y con esto, extraerlo más fácilmente incrementando su factor de recobro. Durante los experimentos de craqueo, se mezcló arena Ottawa con crudo, con maltenos o asfaltenos extraídos del crudo, la mezcla se sometió a una atmósfera inerte compuesta de nitrógeno y calentada a 2°C/min hasta diferentes temperaturas (300°C, 350°C, 400°C y 450°C). Este estudio encontró que los principales productos del craqueo térmico fueron condensables, fracciones no-condensables y un residuo sólido. Análisis próximo, elemental, GC-MS y SIMDIS fueron aplicados con el fin de establecer la composición de los productos de craqueo y determinar el avance de las reacciones. Durante los experimentos de craqueo cada fracción del crudo (maltenos y asfaltenos) produjo especies de más alto y más bajo peso molecular. Por ejemplo, los maltenos produjeron fracciones no condensables (principalmente compuesto por metano CH₄), destilables (una fracción condensable compuesta de especies de máximo 18 carbonos), maltenos de bajo peso molecular (LMWM, una fracción condensable compuesta de especies de máximo 28 carbonos) y asfaltenos. Los asfaltenos formaron coque, LMWM y gases. El pseudo-mecanismo de reacción considera la formación de especies de alto y bajo peso molecular, separa el proceso de destilación del proceso de craqueo térmico y propone nuevos pseudo-componentes como Maltenos*, que representa la fracción de maltenos luego de un proceso de evaporación y que es la fracción disponible para el proceso de craqueo térmico; también LMWM que es una especie mejorada, producto del craqueo térmico de maltenos* y asfaltenos que tuvo un rendimiento de 0.28 g/gtot. El pseudo-mecanismo de reacción también propone parámetros cinéticos para el craqueo térmico de un crudo pesado Colombiano bajo condiciones de combustión in situ a presión atmósferica. Los parámetros
cinéticos se optimizaron minimizando la suma del error cuadrático (SSE) entre los rendimientos experimentales y calculados. Un buen coeficiente de correlación, \( R^2 = 0.97 \), se encontró usando cinéticas de primer orden. Las energías de activación tuvieron valores que variaron entre \( 2.65 \times 10^4 \) y \( 9.67 \times 10^9 \) J/mol, mientras que los factores pre-exponenciales tomaron valores entre \( 2.45 \times 10^{-2} \) to \( 1.07 \times 10^{11} \) s\(^{-1}\).

Palabras clave: Combustión in situ, craqueo térmico, formación de coque, pseudo-mecanismo de reacción, maltenos de bajo peso molecular (LMWM).
Agradecimientos

Agradezco a Colciencias y Ecopetrol por el soporte financiero a esta investigación con el programa: “Herramientas tecnológicas para incrementar el factor de recobro de crudos”, Contrato RC. N° 0264-2013, proyecto 1118-531-30561 “Caracterización mediante técnicas láser de las reacciones químicas de petróleo crudo durante combustión in situ”.

A la Facultad de Minas por la Beca de Exención de Derechos Académicos de Posgrado, otorgado durante los períodos 2012-II a 2014-I.

Al programa Enlaza Mundos por la financiación parcial de la pasantía realizada en la Universidad de Utah entre Abril y Agosto de 2014.

Expreso mi profunda gratitud al Profesor Alejandro Molina, sin su orientación no hubiera sido posible este trabajo. Su trabajo incansable, dedicación y buen actuar no sólo contribuyó a mi formación como investigadora, sino también a mi crecimiento como persona.

Al Profesor Eric Eddings por aceptarme para realizar mi pasantía en la Universidad de Utah y facilitarme los recursos que fueron la clave para el buen termino de este trabajo de investigación.

A Dana Overacker por ser la persona que es, por responder a todas mis dudas y acompañarme en mis jornadas de trabajo.

A todos los compañeros FRUN por aportarle a este trabajo con sus sugerencias y por compartir momentos de alegría. Especial agradecimiento a Luisa Carvajal, por ser mi compañera de batallas.

Por último a mi familia, a mis padres Nora y Javier y mi hermano Daniel por por estar conmigo en todo momento y a mi novio Álvaro, por serlo todo para mí.
# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>RESUMEN</td>
<td>v</td>
</tr>
<tr>
<td>Agradecimientos</td>
<td>vii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>1</td>
</tr>
</tbody>
</table>

1. **Introduction** 2
   1.1. Motivation 2
   1.2. Research objectives 3
     1.2.1. Overall Objective 3
     1.2.2. Specific Objectives 3
   1.3. Description of the Thesis 3

2. **Literature review** 4
   2.1. In-situ combustion (ISC) 4
   2.2. Thermal cracking during in-situ combustion 6
   2.3. Crude oil fractions 6
   2.4. Reaction mechanisms for the thermal cracking of heavy crude oil and coke formation during in-situ combustion 7
   2.5. Reaction mechanisms of other study fields 14
   2.6. Experimental setups to study coke formation from thermal cracking of a heavy crude oil 14

3. **Materials and Methods** 16
   3.1. Castilla crude oil 17
   3.2. Thermal cracking experiments 20
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. Calculation of the Peclet number</td>
<td>75</td>
</tr>
<tr>
<td>C. Micro-GC calibration and measurement methodology</td>
<td>76</td>
</tr>
<tr>
<td>D. Mass balance closure</td>
<td>78</td>
</tr>
<tr>
<td>E. Student’s t-distribution calculations</td>
<td>80</td>
</tr>
<tr>
<td>F. Results of the bootstrap method</td>
<td>81</td>
</tr>
<tr>
<td>G. Chemical composition of LMWM (GC/MS report)</td>
<td>87</td>
</tr>
<tr>
<td>H. Comparison between the experimental and predicted yields</td>
<td>99</td>
</tr>
<tr>
<td>I. Mass transfer considerations</td>
<td>103</td>
</tr>
</tbody>
</table>
List of Figures

2.1. In-situ combustion scheme (modified from [1, 2]) .................................................. 5
2.2. Crude oil classification according to the solubility of the oil in n-heptane (modified from [3]) .......................................................... 7

3.1. TBP curve for Castilla crude oil ................................................................. 19
3.2. Step by step of the experimental methodology ................................................. 21
3.3. Sample carrier ............................................................................................... 22
3.4. Variation of sample temperature with time during quenching of cracking reactions 25
3.5. (a) Experimental setup at Universidad Nacional de Colombia. (b) Experimental setup at University of Utah. ....................................................... 26
3.6. Distribution of one of the optimized kinetic parameter using the bootstrap method 30

4.1. TGA thermogram for crude oil, maltenes and asphaltene concentrate ............... 32
4.2. DTG curves for crude oil, maltenes and asphaltene concentrate ....................... 33
4.3. Variation of the yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of Castilla crude oil. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure. Error bars for the gas fraction are of the order of the data symbols and are not seen at the scale of the figure. Maltenes*, asphaltenes and coke were measured at Colombia; LMWM, distillables and gas were measured at University of Utah. .............................................................. 36
4.4. Variation of the yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of maltenes*. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure. Error bars for the gas fraction are of the order of the data symbols and are not seen at the scale of the figure. Maltenes*, asphaltenes and coke were measured at Colombia; LMWM, distillables and gas were measured at University of Utah.

4.5. Variation of the yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of asphaltenic concentrate. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure. Error bars for the gas fraction are of the order of the data symbols and are not seen at the scale of the figure.

4.6. Comparison of the H/C atomic ratio of the solid residue with H/C atomic ratio of others solid fuels. (Solid fuels references: [4–6]).

4.7. Variation of the yield of coke with temperature during thermal cracking of crude oil, maltenes and asphaltenic concentrate. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure.

4.8. Variation of the yield of LMWM with temperature during thermal cracking of crude oil, maltenes* and asphaltenic concentrate. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure.

4.9. Variation of the cumulative yield of (a) methane (CH$_4$), (b) hydrogen (H$_2$), (c) ethylene (C$_2$H$_4$) and (d) ethane (C$_2$H$_6$) with temperature during thermal cracking of crude oil, maltenes* and asphaltenic concentrate. All the gases start to evolve in the range from 370°C to 400°C except for ethylene that starts at 420°C.

4.10. Variation of the cumulative yield of (a) methane (CH$_4$), (b) hydrogen (H$_2$), (c) ethylene (C$_2$H$_4$) and (d) ethane (C$_2$H$_6$) with temperature during thermal cracking of crude oil up to 700°C. All the gases start to evolve in the range from 370°C to 400°C except for ethylene that starts at 420°C.

4.11. Proposed pseudo-mechanism scheme

4.12. Comparison of the reactions considered in this work and the reactions that some other authors [7–10] proposed.
4.13. Parity plot of the predicted and experimental yields for thermal cracking of crude oil (CO), maltenes* (M) and asphaltenic concentrate (AC) ........................................ 60
4.14. Summarized reaction pathway for the thermal cracking of asphaltenes and H/C atomic ratio for each step ................................................................. 63
C.1. Calibration curve of the studied gases .................................................. 76
D.1. Yield of thermal cracking products for the mass balance closure experiment .......... 78
F.1. Distribution of activation energies for maltenes* reactions ......................... 81
F.2. Distribution of activation energies for asphaltenes reactions ....................... 82
F.3. Distribution of pre-exponential factors for maltenes* reactions ..................... 83
F.4. Distribution of pre-exponential factors for asphaltenes reactions ................... 84
F.5. Scatter plot of maltenes* kinetic parameters ......................................... 85
F.6. Scatter plot of asphaltenes kinetic parameters ....................................... 86
H.1. Experimental and predicted yields for crude oil thermal cracking ................. 99
H.2. Experimental and predicted yields for maltenes* thermal cracking ............... 100
H.3. Experimental and predicted yields for asphaltenes thermal cracking ............. 101
H.4. Experimental and predicted yield of maltenes during evaporation process ...... 102
## List of Tables

2.2. Reaction schemes for crude oil thermal cracking for others study fields 14

3.1. Physical properties of Castilla crude oil [12] 17
3.2. Elemental composition and proximate analysis of Castilla crude oil 18
3.3. Boiling point distribution of Castilla crude oil 20
3.4. SARA fractions of Castilla crude oil, maltenes and asphaltenic concentrate 20
3.5. Nitrogen flow and residence time at the experimental temperatures 23
3.6. Peclet number at different output velocities of exhaust gas 24

4.1. Maximum weight-loss rate for the evaporation and cracking process 33
4.2. Yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of Castilla crude oil 37
4.3. Yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of maltenes* 40
4.4. Yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of asphaltenic concentrate 43
4.5. Elemental analysis of crude oil and solid residues recovered at different temperatures 44
4.6. Proximate analysis of crude oil and solid residues recovered at different temperatures 46
4.7. Yield of distillables with temperature during thermal cracking of crude oil, maltenes* and asphaltenic concentrate 48
4.8. Yield and composition of gases for cracking of crude oil (CO), maltenes* (M) and asphaltenic concentrate (AC) at 450 °C and crude oil at 700°C 53
4.9. Optimized kinetic parameters 59
4.10. Experimental and predicted (in parenthesis) yield in g/gtot according to the proposed pseudo-mechanism for pyrolysis of crude oil (CO), maltenes* (M) and asphaltenic concentrate (AC) at the experimental temperatures 61
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.1.</td>
<td>Constants for the calculation of the Diffusivity of oxygen ($O_2$) in nitrogen ($N_2$) [13]</td>
<td>75</td>
</tr>
<tr>
<td>C.1.</td>
<td>Micro-GC method</td>
<td>77</td>
</tr>
<tr>
<td>D.1.</td>
<td>Yield of thermal cracking products for the mass balance closure experiment with a 95% confidence interval</td>
<td>79</td>
</tr>
<tr>
<td>E.1.</td>
<td>Table of Student t-distribution</td>
<td>80</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1. Motivation

Due to the large deposits of heavy- and extra-heavy-oils and the difficulty to extract them because of their high viscosity, in-situ combustion (ISC) has become an alternative to enhance the recovery factor of these non-conventional oils. ISC is an oil recovery process that consist of injecting hot air to generate heat and gases within the reservoir (in-situ) by burning a portion of the oil [14]. The heat leads to the reduction of the viscosity of the oil, whereas the gas provides a drive mechanism to move the oil to the production well [15]. ISC involves different phenomena such as mass and heat transfer, low temperature oxidation of the liquid phase (LTO, T<350°C) [15], thermal cracking reactions (TC), and high temperature oxidation (HTO, above 500°C) of an hydrocarbon residue where the heat, gases such as carbon oxides and water is formed. The understanding of these reaction stages are important for the correct implementation of the technology at field scale. Cracking reactions play an important role within the ISC process because lead to the formation of the fuel of the process, coke, which is important to the sustainability of the combustion process, and the formation of lower-carbon-number species that implies an upgrading of the oil. Regarding thermal cracking reactions, in the literature there are experimental researches that have identified the main cracking products [16–18], others have proposed reaction mechanisms [7,19–21], and others have proposed kinetic parameters [8,22–24] with the aim of simulating the thermal cracking process and achieving a good prediction of this process under in-situ combustion conditions. Nevertheless, none of these researches have been developed to study the thermal cracking of a Colombian heavy crude oil. This research focuses on studying the thermal cracking process of a Colombian heavy crude oil, by proposing a pseudo-mechanism based on the results of thermal cracking experiments carried out in a semi-batch reactor and a TGA at atmospheric pressure, using Castilla oil, a Colombian heavy crude oil with an API gravity of 13.4. This
work also aims of characterizing the cracking products such as coke, condensable and non-condensable gases by establishing their yields, chemical composition, and by determining some parameters such as H/C atomic ratio and proximate analysis of coke to have an approximation of the advance in the cracking reactions. Furthermore, this study proposes kinetic parameters for each pseudo-reaction that allow to simulate the process with a good agreement between the experimental and simulated results.

1.2. Research objectives

1.2.1. Overall Objective

To establish a reaction mechanism for the coke formation process during the thermal cracking of a Colombian heavy crude oil.

1.2.2. Specific Objectives

1. To develop an experimental setup that allows characterizing the thermal cracking of a heavy crude oil to coke.

2. To propose a reaction mechanism for the thermal cracking of a Colombian heavy crude oil.

1.3. Description of the Thesis

Chapter 2 documents the literature review. Chapter 3 describes the methodology used indicating the conditions of the thermal cracking experiments, the post-experiment analyses, and the steps to optimize kinetic parameters and find confidence intervals. Chapter 4 presents the experimental results, proposes new reaction pseudo-mechanism and the kinetic parameters associated to each reaction and, finally, explains, based on chemical considerations, the experimental results. Chapter 5 lists the conclusions of this work, and makes some recommendations that arise from this study.
Chapter 2

Literature review

This chapter presents general concepts of the in-situ combustion (ISC) process and the thermal cracking reaction zone, that is the main focus of this study. It also shows the general classification of the crude oil according to the solubility of the oil in n-heptane. The chapter summarizes the proposed reaction models for the thermal cracking of a crude oil during the ISC process, and describes some of the reaction schemes proposed for thermal cracking in other study fields. At the end, the chapter lists the experimental setups used to study the coke formation from the thermal cracking of a heavy crude oil.

2.1. In-situ combustion (ISC)

In-situ combustion (ISC) is an Enhanced Oil Recovery (EOR) method that consists of injecting hot air to generate heat and gases within the reservoir (in-situ) by burning a portion of the oil [14]. The heat leads to the reduction of the viscosity of the oil, whereas the gas provides a drive mechanism to move the oil to the production well [15]. During ISC process, the air reacts with the crude oil and a portion of the oil is burnt producing a carbon-rich residue that has low volatility [14], this carbon-rich residue is the fuel of the process and is known as coke. Coke reacts with oxygen generating a combustion front that propagates through the reservoir. The heat and gases produced in the combustion front displace crude oil to the production well. Different reaction zones have been identified for the ISC process, these reaction zones are classified according to its range of temperature. Low temperature oxidation (LTO) dominates below 260°C yielding oxygenated compounds such as alcohols, aldehydes and ketones [25] increasing viscosity and density of the oil [8,26]. Medium-temperature reactions (MTR), up to 450°C, that involve cracking reactions that imply the breaking of carbon-carbon (C-C) and carbon-hydrogen (C-H) bonds, \( \beta \)-scission and condensation of hydrocarbons that lead to the formation of coke. High temperature oxidation reactions (HTO), above 500°C, where oxygen reacts with coke producing heat,
2.1 In-situ combustion (ISC)

water, carbon dioxide (CO₂), and carbon monoxide (CO). Figure 2.1 presents a simplified scheme of the reaction zones formed during in-situ combustion process.

![In-situ combustion scheme](image)

**Figure 2.1**: In-situ combustion scheme (modified from [1, 2])

Starting from the injection well, the zones represented in Figure 2.1 are:

1. Burnt zone: The burnt zone contains the injected air and may contain small amounts of residual unburned organic solids [2, 27].

2. Combustion zone: It is in this zone where the injected oxygen and the solid fuel (coke) react exothermically, and high temperature oxidation occurs generating heat and combustion products, such as carbon oxides and water [2, 27].

3. Thermal cracking/vaporization zone: Downstream of the combustion zone is located the thermal cracking zone. In this zone the heat generated in the combustion process causes the components of the crude oil to vaporize [14]. Furthermore as it is a oxygen-free region, the breaking of carbon-carbon (C-C) and carbon-hydrogen (C-H) bonds dominate. Thermal cracking process leads to the formation of coke and low-carbon number hydrocarbons. The vaporized and the low-carbon number hydrocarbons are transported downstream by the combustion gases [14].

4. Mobile oil zone: In the mobile oil zone some of the hydrocarbons vaporized condense and dissolve in the crude. This region contains steam, oil, water, and gases. At the leading edge of this zone
where the temperature is lower than the temperature condensation of steam, a hot water bank is formed. An oil bank proceeds the water bank. This zone contains all the oil that have been displaced from upstream zones [14].

5. Initial oil zone: The initial oil zone is a region that has not been affected by the combustion process, except for a possible increase in gas saturation due to flow of combustion gases (CO₂, CO and N₂) [14].

2.2. Thermal cracking during in-situ combustion

As the reservoir temperature raises, the oil undergo a chemical change called pyrolysis. Pyrolysis is the chemical alteration of hydrocarbons under the effect of heat in an inert atmosphere. Some of the reactions that a fuel undergoes during pyrolysis are: dehydrogenation, cracking and condensation. In the literature about in-situ combustion, pyrolysis process is often referred to as thermal cracking, as this study is part of an in-situ combustion research project, then this document will refer with the term «thermal cracking».

Thermal cracking reactions have paramount importance because they are responsible for the formation of coke, the fuel of the in-situ combustion. The thermal cracking zone is located downstream of the combustion zone, as Figure 2.1 shows. As during the combustion zone the oxygen reacts with coke, then the subsequent region is an oxygen free region where cracking reactions dominate. The reactions associated with thermal cracking are: dehydrogenation, cracking and condensation. In the dehydrogenation reactions hydrogen atoms are removed from the hydrocarbon molecules. In cracking reactions, the carbon-carbon (C-C) bonds of the hydrocarbons are broken forming lower-carbon number (smaller) hydrocarbon molecules. For condensation reactions, the number of carbon atoms in the molecules increases leading to the formation of heavier hydrocarbons. Cracking reactions are usually initiated by the cleavage of the carbon-carbon bond, followed by hydrogen abstraction. The molecules that recombine to form heavier molecules eventually leading to the formation of coke. Coke is not pure carbon, but a hydrogen-deficient organic material with a hydrogen-to-carbon atomic ratio (H/C) ranged from 0.6 to 1.6 [14, 25, 27–29].

2.3. Crude oil fractions

Petroleum is a complex mixture containing many components with different molecular sizes. The variety is so great that a complete compound-by-compound description is unlikely [27]. Nevertheless, classifying a crude oil according to its physical and chemical properties could be a way to achieve an
2.4 Reaction mechanisms for the thermal cracking of heavy crude oil and coke formation during in-situ combustion

insight into its composition. e.g., the boiling point distribution of a crude oil provide and approximation of the molecular weight of its components, API gravity suggests whether a crude oil is heavy or light. Regarding chemical composition, crude oil components could be classified into two pseudo-components according to its solubility in n-heptane. Maltenes is the name for the soluble fraction in n-heptane and asphaltenes are the n-heptane insoluble fraction. Maltenes are also classified into three different hydrocarbon types: saturates, aromatics and resins after a chromatographic separation. According to this, crude oil could be chemically classified as Saturates, Aromatics, Resins and Asphaltenes, SARA fractions. Figure 2.2 summarizes this chemical classification of a crude oil.

![Crude oil classification diagram](image)

**Figure 2.2**: Crude oil classification according to the solubility of the oil in n-heptane (modified from [3])

2.4. Reaction mechanisms for the thermal cracking of heavy crude oil and coke formation during in-situ combustion

Table 2.1 summarizes some of the proposed reaction mechanisms for thermal cracking and coke formation during in-situ combustion. According to the reaction mechanisms presented in Table 2.1, cracking reactions produce lighter molecules, whereas reactions such as polymerization and condensation produce heavier molecules from lighter fractions. Coke is a product of the mentioned processes.

The proposed reaction mechanisms have evolved over time, the first thermal cracking experiments aimed to characterize the upgrading of heavy oil during thermal cracking reactions. Therefore, rather than proposing a chemical explanation of the cracking process, those studies identified thermal cracking products [11]. Some of the pseudo-components that authors such as Egloff and Morrell [16], Bunger et al. [18], Speight [17] identified were: Distillate, non-condensable fraction (gas), coke, light oil and resins as Table 2.1 shows.

With time the focus of thermal cracking studies shifted toward the design of the in-situ combustion
processes [11] which required new reaction mechanisms and kinetics parameters. Most of the proposed mechanism schemes used pseudo-components. Authors such as Burger and Sahuquet [7], Hayashitani et al. [19], Lin et al. [20] and Phillips et al. [21] used pseudo-components such as light oils, middle oils, heavy oils and volatiles. These early studies suggested that the assumption that asphaltenes are the only precursors of coke formation is not entirely accurate [4] and that asphaltenes produce lighter species, such as heavy oil and volatiles [7,19].

Other authors such as Belgrave et al. [8] and Millour et al. [30] proposed reaction mechanisms using pseudo-components (maltenes and asphaltenes) classified in accordance with their solubility in solvents.

Banerjee et al. [31], Mazza and Cormack et al. [32], and Freitag et al. [33] proposed more detailed cracking mechanism that used SARA fractions. According to the chemistry of these mechanisms: saturates cyclize yielding aromatics that undergo condensation reactions to produce resins. Resins also condensate producing asphaltenes that finally lead to coke.

Since 1990 the interests in mechanisms able to predict thermal cracking during ISC has remained high. The researchers have also focused on the prediction of kinetic parameters: Murugan et al. [23] provided a range for the activation energies for thermal cracking of Fosterton oil (7 to 129 kJ/mol) and its asphaltene (50 to 183 kJ/mol). Jia et al. [22] proposes a reaction scheme and expression for reaction coefficients as presented in Table 2.1. Kapadia et al. [24] improved Belgrave’s model by considering the formation of different gaseous species due to cracking of asphaltenes: hydrogen (H$_2$), methane (CH$_4$), hydrogen sulfide (H$_2$S), carbon monoxide (CO), carbon dioxide (CO$_2$) and heavy molecular weight gases (HMWG); along with coke production. This study also proposed kinetic parameters for each reaction as Table 2.1 shows.
Table 2.1: Summary of thermal cracking mechanism schemes. Modified from Kapadia et al. 2015 [11]

<table>
<thead>
<tr>
<th>Reference</th>
<th>Components</th>
<th>Proposed reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Egloff and Morrel. 1927 [16]</td>
<td>• Distillate&lt;br&gt;• Non-condensable fraction&lt;br&gt;• Coke</td>
<td>–</td>
</tr>
<tr>
<td>Speight. 1970 [17]</td>
<td>• Light oil&lt;br&gt;• Resins&lt;br&gt;• Coke&lt;br&gt;• Gas</td>
<td>–</td>
</tr>
<tr>
<td>Bunerger et al. 1976 [18]</td>
<td>• Gases (C₅ and lighter) &lt;br&gt;• Liquid condensate (C₆ to 535 boiling fraction)&lt;br&gt;• Coke</td>
<td>–</td>
</tr>
<tr>
<td>Burger and Sahuquet et al. 1971 [7]</td>
<td>• Hydrocarbons&lt;br&gt;• Resins&lt;br&gt;• Asphaltenes&lt;br&gt;• Coke&lt;br&gt;• Volatile products</td>
<td>Hydrocarbons → resins&lt;br&gt;Resins → hydrocarbons&lt;br&gt;Asphaltenes → asphaltenes&lt;br&gt;Asphaltenes → coke&lt;br&gt;Asphaltenes → volatile products → hydrocarbons (Model A-1)</td>
</tr>
<tr>
<td>Hayashtani et al. 1978 [19]</td>
<td>• Coke&lt;br&gt;• Asphaltenes&lt;br&gt;• Heavy oils (boiling point 400°C +)</td>
<td>Asphaltenes → coke&lt;br&gt;Asphaltenes → heavy oils&lt;br&gt;Heavy oils → asphaltenes</td>
</tr>
</tbody>
</table>

(Continued on next page)
<table>
<thead>
<tr>
<th>Reference</th>
<th>Components</th>
<th>Proposed reaction scheme</th>
</tr>
</thead>
</table>
| Lin et al. 1984 [20] | - Middle oils (boiling point 200-400°C)  
- Light oils (boiling point 20-200°C)  
- Gas                      | Heavy oils→ distillables  
Distillables→ heavy oils  
Asphaltenes→ distillables  
where distillables = gas + light oils + middle oils  
*Model A*                                                                 |
|                     | Light-oil                                                               | *Model B*                                                                                 |
- Medium-oil  
- Light-oil  
- Coke  
- Asphaltenes  
- Heavy oils (boiling point 400°C +)  
- Middle oils (boiling point 200-400°C)  
- Light oils (boiling point 20-200°C)  
- Gas | Heavy-oil→ coke+light-oil  
Light-oil→ coke  
*Model B*  
Heavy-oil→ coke+medium-oil+light-oil  
Medium-oil→ light-oil + coke  
Asphaltenes→ coke  
Asphaltenes → heavy oils  
Heavy oils→ asphaltenes  
Heavy oils→ distillables  
Distillables→ heavy oils  
where distillables = gas + light oils + middle oils  
*Model B*  
Asphaltenes → coke  
Asphaltenes → heavy oils  
Asphaltenes → gas  
Heavy oils→ asphaltenes  
(Continued on next page)
2.4 Reaction mechanisms for the thermal cracking of heavy crude oil and coke formation during in-situ combustion

<table>
<thead>
<tr>
<th>Reference</th>
<th>Components</th>
<th>Proposed reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgrave et al. 1993 [8]</td>
<td>Maltenes</td>
<td>Middle oils $\rightarrow$ heavy oils</td>
</tr>
<tr>
<td></td>
<td>Asphaltenes</td>
<td>Light oils $\rightarrow$ middle oils</td>
</tr>
<tr>
<td></td>
<td>Coke</td>
<td>Heavy oils $\rightarrow$ middle oils</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>Middle oils $\rightarrow$ light oils</td>
</tr>
<tr>
<td></td>
<td>Maltenes $\rightarrow$ asphaltenes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Asphaltenes $\rightarrow$ coke</td>
<td></td>
</tr>
<tr>
<td>Banerjee et al. 1986 [31]</td>
<td>Saturates</td>
<td>Saturates $\rightarrow$ paraffins</td>
</tr>
<tr>
<td></td>
<td>Paraffins</td>
<td>Paraffins $\rightarrow$ olefins</td>
</tr>
<tr>
<td></td>
<td>Olefins</td>
<td>Olefins $\rightarrow$ lower hydrocarbons</td>
</tr>
<tr>
<td></td>
<td>Lower hydrocarbons (lower HC)</td>
<td>Lower hydrocarbons $\rightarrow$ hydrogen</td>
</tr>
<tr>
<td></td>
<td>Hydrogen (H$_2$)</td>
<td>Lower hydrocarbons $\rightarrow$ hydrogen</td>
</tr>
<tr>
<td></td>
<td>Napthenes</td>
<td>Saturates $\rightarrow$ napthenes</td>
</tr>
<tr>
<td></td>
<td>Cyclo olefins</td>
<td>Napthenes $\rightarrow$ cyclo olefins+lower HC +H$_2$</td>
</tr>
<tr>
<td></td>
<td>Small aromatics</td>
<td>Cyclo olefins $\rightarrow$ small aromatics</td>
</tr>
<tr>
<td></td>
<td>Resins</td>
<td>Small aromatics $\rightarrow$ resins + large aromatics</td>
</tr>
<tr>
<td></td>
<td>Large aromatics</td>
<td>Resins $\rightarrow$ large aromatics + asphaltenes</td>
</tr>
<tr>
<td></td>
<td>Asphaltenes</td>
<td>Large aromatics $\rightarrow$ coke</td>
</tr>
<tr>
<td></td>
<td>Maltenes $\rightarrow$ large aromatics</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td>Saturate $\rightarrow$ aromatic</td>
</tr>
</tbody>
</table>

(Continued on next page)
<table>
<thead>
<tr>
<th>Reference</th>
<th>Components</th>
<th>Proposed reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Resin</td>
<td>Aromatic→ volatiles</td>
<td></td>
</tr>
<tr>
<td>• Asphaltene</td>
<td>Aromatic→ resins</td>
<td></td>
</tr>
<tr>
<td>• Volatiles (boiling point less than 105°C)</td>
<td>Resins→ volatiles</td>
<td></td>
</tr>
<tr>
<td>Freitag et al. 2006 [33]</td>
<td>• Saturates</td>
<td>100 Saturates→ 8 gas+ 62 light ends +30 aromatics</td>
</tr>
<tr>
<td></td>
<td>• Aromatics</td>
<td>100 Aromatics→ 1 gas+ 18 light ends +3 saturates</td>
</tr>
<tr>
<td></td>
<td>• Resins</td>
<td>+ 78 resins</td>
</tr>
<tr>
<td></td>
<td>• Asphaltenes</td>
<td>100 Resins→ 5 gas+ 16 light ends + 22 saturates</td>
</tr>
<tr>
<td></td>
<td>• Coke</td>
<td>+ 28 aromatics + 29 asphaltene</td>
</tr>
<tr>
<td></td>
<td>• Light ends</td>
<td>100 Asphaltenes→ 4 gas+ 2 light ends + 10 saturates</td>
</tr>
<tr>
<td></td>
<td>+ 4 aromatics + 3 resins + 77 coke</td>
<td></td>
</tr>
<tr>
<td>Jia et al. 2009 [22]</td>
<td>• C_{mal,R}: Reactive maltenes content</td>
<td>C_{mal,R} \rightarrow \overset{k_H}{aC_{asp,P}} + (1-a)C_{gas}</td>
</tr>
<tr>
<td></td>
<td>• C_{asp,R}: Reactive asphaltene content</td>
<td>C_{asp,R} \rightarrow \overset{k_A}{mC_{asp,P}} + nC_{mal,P} + (1-m-n)C_{gas}</td>
</tr>
<tr>
<td></td>
<td>• C_{gas}: Gas content</td>
<td>C_{asp,P} \rightarrow \overset{\infty}{(1-y)C_{coke} + yC_{mal,P}}</td>
</tr>
<tr>
<td></td>
<td>• C_{mal,P}: Product maltenes content</td>
<td>Where k_H = 2.96 \times 10^{13} \times e^{-2.33 \times 10^5/RT}</td>
</tr>
<tr>
<td></td>
<td>• C_{asp,P}: Product asphaltenes content</td>
<td>Where k_A = 1.17 \times 10^7 \times e^{-1.31 \times 10^5/RT}</td>
</tr>
<tr>
<td></td>
<td>• C_{coke}: Coke content</td>
<td>Where a=0.84, m=0.81, n=0.12</td>
</tr>
<tr>
<td>Kapadia et al. 2012 [24]</td>
<td>• Maltenes</td>
<td>2.68 Maltenes $k_1$ asphaltenes</td>
</tr>
<tr>
<td></td>
<td>• Asphaltenes</td>
<td>Asphaltenes $k_2$ 11.89 coke</td>
</tr>
<tr>
<td></td>
<td>• Coke</td>
<td>Asphaltenes $k_3$ 7.44 H₂</td>
</tr>
<tr>
<td></td>
<td>• Hydrogen (H₂)</td>
<td>Asphaltenes $k_4$ 9.7 CH₄</td>
</tr>
</tbody>
</table>

(Continued on next page)
2.4 Reaction mechanisms for the thermal cracking of heavy crude oil and coke formation during in-situ combustion

<table>
<thead>
<tr>
<th>Reference Components</th>
<th>Proposed reaction scheme</th>
<th>$A(h^{-1})$ and $k(J/mol)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH$_4$)</td>
<td>Asphaltenes$^{k_3}$ 5.57 CO</td>
<td>$A_1=4.9 \times 10^{16}$ $k_1=2.3 \times 10^5$</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>Asphaltenes$^{k_4}$ 3.54 CO$_2$</td>
<td>$A_2=1.3 \times 10^{14}$ $k_2=1.2 \times 10^5$</td>
</tr>
<tr>
<td>Carbon dioxide (CO$_2$)</td>
<td>Asphaltenes$^{k_5}$ 3.54 H$_2$S</td>
<td>$A_3=9.2 \times 10^3$ $k_3=9.9 \times 10^4$</td>
</tr>
<tr>
<td>Hydrogen sulfide (H$_2$S)</td>
<td>Asphaltenes$^{k_8}$ 3.76 HMWG</td>
<td>$A_4=1.0 \times 10^7$ $k_4=1.1 \times 10^5$</td>
</tr>
<tr>
<td>High molecular weight gases (HMWG)</td>
<td>where $A(h^{-1})$ and $k(J/mol)$</td>
<td>$A_5=2.6$ $k_5=4.9 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_6=7.8 \times 10^{-2}$ $k_6=2.3 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_7=1.4 \times 10^5$ $k_7=9.7 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_8=2.5 \times 10^{14}$ $k_8=2.0 \times 10^5$</td>
</tr>
</tbody>
</table>
2.5. Reaction mechanisms of other study fields

Other researches aimed to study thermal cracking behavior of heavy crude oils for other study fields. Those studies have proposed reaction mechanisms mainly for thermal cracking of asphaltenes. Some of these proposed reaction mechanisms were the mechanisms of Martínez et al. [4] and Trejo et al. [10]. These reaction mechanisms present the behavior of asphaltenes during thermal cracking. Table 2.2 shows Martínez et al. and Trejo et al. reaction schemes.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Components</th>
<th>Proposed reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martínez et al. (1997) [9]</td>
<td>• Asphaltenes</td>
<td>Asphaltenes $\rightarrow$ oil + gas</td>
</tr>
<tr>
<td></td>
<td>• Oil</td>
<td>Asphaltenes $\rightarrow$ coke</td>
</tr>
<tr>
<td></td>
<td>• Coke</td>
<td>Oil $\rightarrow$ coke</td>
</tr>
<tr>
<td>Trejo et al. (2014) [10]</td>
<td>• Asphaltenes</td>
<td>Asphaltenes $\rightarrow$ coke</td>
</tr>
<tr>
<td></td>
<td>• Maltenes</td>
<td>Asphaltenes $\rightarrow$ maltenes</td>
</tr>
<tr>
<td></td>
<td>• Coke</td>
<td>Asphaltenes $\rightarrow$ gases</td>
</tr>
<tr>
<td></td>
<td>• Gases</td>
<td>Asphaltenes $\rightarrow$ gases</td>
</tr>
</tbody>
</table>

2.6. Experimental setups to study coke formation from thermal cracking of a heavy crude oil

Many areas of study, including in-situ combustion, aim to understand the thermal decomposition of crude oil, its fractions, and the coke formation process. In order to achieve this goal, studies have used different lab-scale reactor configurations, thermogravimetric analysers and other instruments. Some of the most common setups are presented below:

1. Thermogravimetric analysis:

Thermogravimetric (TGA) is an analytical method that describes the thermal behavior of substances during programmed temperatures changes by providing weight loss data with respect to time or temperature [4,34]. By using TGA analysis, studies [3,35–42] have provided a good insight into thermal decomposition of crude oil and its fractions and coke formation. Kinetic models and kinetic parameters have also been proposed from the analysis of TGA experiments [23,43–48].

2. Batch or semi-batch reactors:
Batch- or semi-batch-reactor experiments have a different purpose in comparison with combustion-tube tests as they are used to evaluate kinetic parameters of the crude oil and its fractions. Batch and semi-batch setup have not an exclusive use for in-situ combustion studies.

It is important to clarify that both setups use semi-batch-reactor configurations, because during the test the nitrogen is always flowing into the reactor. However, during the experiment named as batch, the condensable products are not collected and with this the reactor is batch for the oil phase. In a semi-batch-reactor experiment condensable products are collected and the non-condensable gases are analysed. Condensable fractions are normally collected in a cold trap set at temperatures below 0°C [49–54]. The deposited coke deposited can be analysed after the run in both setups. While most setups [19,21,55,56] use electrical resistances to heat the reactors, recently Bazargan et al. [57] used induction heating to expedite the cooling process of the reactor.

In these experimental setups the sample is placed inside the reactor; the sample could be the whole crude oil, maltenes or asphaltenes. When maltenes or asphaltenes are used as sample, the fractions are first separated by filtration using n-heptane or n-pentane as solvent [19,22,58].

The experiment could be isothermal or non-isothermal. During isothermal experiments the reactor's temperature is raised up to the desired point and then the reaction is stopped at different stages of the cracking process. Most authors in this field [10,19,21,55,59,60] report the results as concentration versus reaction-time. Some common temperatures for isothermal cracking experiments are carried out between 300°C and 500°C [10,19,21,33,49,51,54–56,59–63]. In a non-isothermal test, the temperature increases at a constant heating rate until a desired final temperature [50,52,53]. Heating rates have been reported from 1°C/min up to 8°C/min [61,64,65].

3. Combustion-tube test:

Combustion-tube tests are commonly used for in-situ combustion characterization. This setup provides a base to approximate information that it is difficult to establish during pilot or field tests [66] such as: the amount of fuel deposited and/or burned during combustion, air requirements, factor recovery, temperature profiles and combustion front propagation. During combustion-tube tests a mixture of sand, clay, water and crude oil is packed inside the reactor. This mixture is burned by heating the top of the tube, while the temperature along the reactor is monitored. Produced gases are continuously monitored at the exit of the reactor. Combustion tubes are designed to work at high temperatures (up to 900°C) and high pressures (100 atm) [67] to simulate reservoir conditions. After the runs, post-experiment analyses are performed to study the deposited coke [28,65,68,69].
Chapter 3

Materials and Methods

Oil from Castilla well was used in the experiments, as well as, maltenes and asphaltenes separated from this oil. Castilla Oil is composed of 81% wt. maltenes and 15% wt. asphaltenes, has a density of 0.98 g/cc at 15°C (13.4 API), a viscosity of 971.9 cSt at 50°C [12]. Asphaltenes and maltenes were separated from Castilla oil according to the standardized ASTM D-6560 method [70]. The samples charged to the thermal cracking reactor were a mixture of Ottawa sand (with a size range of 250 μm-500 μm) and crude oil, maltenes or asphaltenes in a proportion of 20% wt.-80% wt. respectively. This study carried out the experimental procedures at two places. At Universidad Nacional de Colombia -Sede Medellín-, where the mixtures of Ottawa sand with crude oil, maltenes and asphaltenic concentrate were placed under nitrogen flow with an average velocity of 0.07 m/s in a 2.54-cm ID horizontal furnace. The samples were heated at 2°C/min up to a final temperature that varied between 300°C and 450°C. The reactor, made of stainless steel 304, was cooled down to atmospheric temperature at a rate of 19°C/min to quench thermal cracking reactions. During these experiments volatile products were released, the condensable fraction of these volatile products was collected in a cold trap set at -20°C and weighted.

The experiments at University of Utah proceed under the same conditions, i.e., same heating rate, samples and nitrogen linear velocity. Nevertheless, in comparison with Universidad Nacional de Colombia experiments, during University of Utah experiments the condensable fraction of volatile products was collected by a modular system formed by a warm (40°C) and a cold (-12°C) vessel where bubblers with isopropanol captured condensable fractions. With the study of the non-condensable fraction using a micro-GC, this study could establish yield and composition of this non-condensable fraction. The study that this document presents also performed some post-experiment analyses: condensable fractions were analysed by SIMDIS test to determine the boiling point distribution and propose a range for the molecular weight of this sample. This sample was also analysed with a GC-MS to characterize
3.1 Castilla crude oil

The samples used in this research were Castilla oil, maltenes and asphaltenic concentrate. Some physical properties of Castilla oil taken from Navarro et al. [12] are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C, g/cc</td>
<td>0.98</td>
</tr>
<tr>
<td>°API</td>
<td>13.4</td>
</tr>
<tr>
<td>Viscosity at 50°C, cSt</td>
<td>971.9</td>
</tr>
<tr>
<td>Viscosity at 80°C, cSt</td>
<td>144.6</td>
</tr>
</tbody>
</table>

Chemical properties of Castilla crude oil, maltenes and asphaltenic concentrate are presented in tables 3.2, 3.3 and 3.4 and Figure 3.1. Table 3.2 presents elemental composition and proximate analysis of Castilla oil. The analyses were obtained by applying the ASTM D-5373-08 method in a LECO TruSpec Micro equipment, and by using a Q-50 thermobalance respectively. Figure 3.1 and Table 3.3 present the boiling point distribution of Castilla crude oil provided by a simulated distillation test (SIMDIS), applying the ASTM D2887 standarized test using an Agilent 7890A GC. Table 3.4 presents SARA distribution of crude oil and its fractions. These SARA fractions were found by applying the standard test method IP 469 using a IATROSCAN MK-6 equipment.
Table 3.2: Elemental composition and proximate analysis of Castilla crude oil

<table>
<thead>
<tr>
<th>Elemental composition</th>
<th>(wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>82.3</td>
</tr>
<tr>
<td>H</td>
<td>9.2</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>2.4</td>
</tr>
<tr>
<td>O*</td>
<td>6.08</td>
</tr>
<tr>
<td>H/C: atomic ratio</td>
<td>1.34</td>
</tr>
<tr>
<td>S/C: atomic ratio</td>
<td>0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>(wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>5</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>84</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>11</td>
</tr>
<tr>
<td>Ash</td>
<td>0</td>
</tr>
</tbody>
</table>

*The oxygen content was calculated by difference
3.1 Castilla crude oil

Figure 3.1: TBP curve for Castilla crude oil
Table 3.3: Boiling point distribution of Castilla crude oil

<table>
<thead>
<tr>
<th>Weight Percent (%)</th>
<th>Boiling Point (°C)</th>
<th>Compound</th>
<th>Molecular Weight (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP</td>
<td>172.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>175.71</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>242.80</td>
<td>C13</td>
<td>184.5</td>
</tr>
<tr>
<td>10</td>
<td>292.06</td>
<td>C16</td>
<td>226.43</td>
</tr>
<tr>
<td>15</td>
<td>328.15</td>
<td>C19</td>
<td>268.62</td>
</tr>
<tr>
<td>20</td>
<td>362.84</td>
<td>C21</td>
<td>329.63</td>
</tr>
<tr>
<td>25</td>
<td>397.49</td>
<td>C25</td>
<td>352.76</td>
</tr>
<tr>
<td>30</td>
<td>429.85</td>
<td>C28</td>
<td>394.76</td>
</tr>
<tr>
<td>35</td>
<td>463.60</td>
<td>C31</td>
<td>436.78</td>
</tr>
<tr>
<td>40</td>
<td>509.73</td>
<td>C37</td>
<td>521.05</td>
</tr>
<tr>
<td>45</td>
<td>558.24</td>
<td>C45</td>
<td>633.26</td>
</tr>
<tr>
<td>50</td>
<td>605.52</td>
<td>C53</td>
<td>745.47</td>
</tr>
<tr>
<td>55</td>
<td>658.65</td>
<td>C74</td>
<td>1040.01</td>
</tr>
<tr>
<td>60</td>
<td>710.13</td>
<td>C94</td>
<td>1320.56</td>
</tr>
<tr>
<td>FBP</td>
<td>720</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

% Recovery 61.05

% Residue 38.95

Table 3.4: SARA fractions of Castilla crude oil, maltenes and asphaltene concentrate

<table>
<thead>
<tr>
<th>Fraction (wt. %)</th>
<th>Castilla crude oil</th>
<th>Maltenes</th>
<th>Asphaltenic concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>9.69</td>
<td>14.71</td>
<td>18.45</td>
</tr>
<tr>
<td>Aromatics</td>
<td>19.47</td>
<td>26.37</td>
<td>0</td>
</tr>
<tr>
<td>Resins</td>
<td>51.42</td>
<td>58.92</td>
<td>28.86</td>
</tr>
<tr>
<td>TOTAL maltenes</td>
<td>80.58</td>
<td>100</td>
<td>47.31</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>19.42</td>
<td>0</td>
<td>52.69</td>
</tr>
</tbody>
</table>

3.2. Thermal cracking experiments

This section summarizes the experimental-methodology and explains each item of this methodology. Figure 3.2 presents step by step the experimental-methodology.
3.2 Thermal cracking experiments

Maltenes and asphaltenes separation
Sample preparation (crude oil/maltenes/asphaltenic concentrate/sand)
Sample loading into the reactor
Sample heating at 2°C/min up to 300°C, 350°C, 400°C and 450°C under nitrogen atmosphere
Quenching of the reactions
Recovery and weight determination of the cracking products (condensables and cracking residue)
Post-experiment analyses to establish the advance in the reactions
Results analysis
Reaction mechanism proposal and determination of the kinetic parameters

Figure 3.2: Step by step of the experimental methodology

3.2.1 Sample preparation

Maltenes and asphaltenic concentrate were separated from Castilla crude oil according to the standardized ASTM D6560. This method separates fractions of crude oil according to their solubility in n-heptane. In agreement with the ASTM standard, for each 0.8 g of sample were added between 25 mL and 30 mL of n-heptane and then the mixture was boiled under reflux for 60 minutes and stored in a dark place for 90 minutes. After that the mixture was filtered to separate solubles and insolubles in n-heptane. The insoluble fraction in n-heptane was the asphaltenic concentrate. This insoluble fraction was boiled again with n-heptane under reflux for a period of time not less than 60 minutes or until n-heptane passes through the filter without color. The aim of this step was to remove most of
the remnant-maltenes in the n-heptane insoluble fraction. Afterward the remnant-insoluble fraction was
dried for 30 minutes at 110°C to evaporate n-heptane. The soluble fraction in n-heptane was recovered
removing n-heptane by evaporation in a rotovapor.

Once the crude oil fractions were separated, the mixtures sand/oil, sand/maltenes or sand/asphaltene
concentrate were prepared and charged in the reactor. These samples were 20% wt. oil 80% wt sand.
This study used the mixtures of sand and oil because it was easier to handle a solid sample instead
of a liquid sample, also because it was a way to simulate crude oil in a reservoir. The proportion
20% oil-80% sand was selected because with a higher proportion of oil (>20%) the sample became
too compact hampering the distribution of the sample inside the sample carrier, and with a lower
proportion (<20%) there was not enough quantity of oil to perform the post-experiment analysis.

Ottawa sand was used as surrogate of the sand of the reservoir, following other authors [52, 53] who
also used this material for their ISC experiments. The Ottawa sand used the experiments of this study
had a particle size of 250 µm-500 µm. This particle size was chosen since it was the characteristic
particle size of Colombian Chichimene-29 reservoir, in agreement with the information provided by
the Colombian Petroleum Institute (ICP). Figure 3.3 shows an image the sample placed on the sample
carrier.

![Sample carrier](image)

**Figure 3.3:** sample carrier

### 3.2.2. Heating rate and maximum experimental temperature

The heating rate of the experimental runs was established based on the information that Abu-Khamsin
et al. [53] presented, that indicates that the heating rate of the in-situ combustion is in a range between
0.18 K/min and 0.46 K/min. Besides, Fassihi et al. [71] indicated that the heating rates in the reservoir,
are believed to be in the range of 2°C/min. Thus, the heating rate was selected as 2°C/min because
it is close to the range proposed by Abu-Khamsin et al. [53] without implying and excessive amount
of time, and it is in accordance with Fassihi et al. [71].

The experimental temperatures were selected considering the information provided by different works [8, 14, 19, 25, 29, 53] that indicate that the thermal cracking reactions take place in a middle temperature region between 300°C and 450°C. For this reason, the experiments were run from 300°C to 450°C with analysis of the cracking products every 50°C.

3.2.3. Residence time inside the reactor

This study considered as residence time, the time required by the nitrogen flow to cross the reactive region, i.e. the zone where the mixture oil/sand was located. This work estimated the residence time by taking into account the nitrogen flow at the entrance of the reactor, the temperature at the reaction zone and the length on which was placed the sample inside the sample carrier.

The nitrogen flow at the entrance of the reactor was controlled with a pressure regulator set at 132 psi and a critical flow orifice (CFO) with an orifice diameter of 0.08 mm. The flow of nitrogen was 573 cm³/min at atmospheric conditions (25°C and 1 atm). The nitrogen flow inside the reactor varied depending on the experiment temperature. Table 3.5 presents nitrogen flow, the experimental temperatures, and residence times. The average residence time was 2.2 s with a range from 1.9 s to 2.4 s. Appendix A presents more details about the residence time calculation.

<table>
<thead>
<tr>
<th>T_{final} (°C)</th>
<th>F_{final} (P= 1 atm) (cm³/min)</th>
<th>Residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1153.4</td>
<td>2.4</td>
</tr>
<tr>
<td>350</td>
<td>1254.0</td>
<td>2.2</td>
</tr>
<tr>
<td>400</td>
<td>1354.7</td>
<td>2.0</td>
</tr>
<tr>
<td>450</td>
<td>1455.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

3.2.4. Quenching of thermal cracking reactions

The reactor, made of stainless steel 304, was cooled down to atmospheric temperature at an average rate of 19°C/min to quench thermal cracking reactions. The quenching consisted of opening the outlet of the reactor, and moving the horizontal tube out of the furnace. To evaluate the possible diffusion of oxygen from air into the reactor during quenching, the Peclet number, Pe, a dimensionless number that relates advection with diffusion, was computed. For the interest of this study, it related the flow of gas that leaved the reactor and the diffusion of oxygen through this gas. The composition of the
gas was assumed mainly as N$_2$. The Peclet number was calculated with Equation 3.1.

$$ Pe = \frac{LU}{D} \quad (3.1) $$

where $L$ is the internal diameter of the horizontal furnace (2.24 cm); $U$ is the output velocity of the gas at atmospheric pressure and at the maximum temperature of the run and $D$ is the diffusivity of oxygen in nitrogen. Appendix B presents the details of the calculation of the Peclet number.

Table 3.6 presents the values for Peclet number at the different output velocities of exhaust gas. Peclet number was considerably greater than 1 in all the studied cases. This suggests that oxidation of the sample because of the diffusion of oxygen from air during the quenching period could be neglected.

<table>
<thead>
<tr>
<th>$T_{\text{final}}$ ($^\circ$C)</th>
<th>$F_{\text{final}}$ (P= 1 atm)(cm$^3$/min)</th>
<th>$U$ (cm/s)</th>
<th>$D_{O_2-N_2}$ (cm$^2$/s)</th>
<th>Pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>600</td>
<td>5.1</td>
<td>0.2</td>
<td>55.2</td>
</tr>
<tr>
<td>300</td>
<td>1153.4</td>
<td>9.8</td>
<td>0.7</td>
<td>32.3</td>
</tr>
<tr>
<td>350</td>
<td>1254.0</td>
<td>10.6</td>
<td>0.8</td>
<td>30.1</td>
</tr>
<tr>
<td>400</td>
<td>1354.7</td>
<td>11.5</td>
<td>0.9</td>
<td>28.3</td>
</tr>
<tr>
<td>450</td>
<td>1455.3</td>
<td>12.3</td>
<td>1.0</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Figure 3.4 presents the variation of reactor temperature with time during quenching. The cooling of the reactor from 450$^\circ$C to 100$^\circ$C, 100$^\circ$C was considered a temperature at which there were no reactions, took about 18 minutes which is much lower than the length of the experiment (4 hours).
3.2 Thermal cracking experiments

3.2.5. Units of the experimental setup

Figure 3.5 presents the experimental setups at Universidad Nacional de Colombia -Sede Medellín- and at University of Utah. The experiments at University of Utah proceeded under the same conditions of the experiments at Universidad Nacional de Colombia. The difference between these experimental setups was the system to collect condensable fractions and the analysis of the non-condensable fraction. Experiments at University of Utah allowed a more sophisticated and accurate analysis of the gas phase.
Figure 3.5: (a) Experimental setup at Universidad Nacional de Colombia. (b) Experimental setup at University of Utah.

The different sections of the experimental setup are described below.

1. Gas inlet:

A nitrogen gas cylinder, with a purity of 99.95%, a regulator set at 132 psi, and a critical flow orifice (CFO) with an orifice diameter of 0.08 mm were the elements that composed the gas inlet unit. 573 cm³/min was the set inlet gas flow at atmospheric conditions (25°C, 1 atm), as Section 3.2.3 indicated.

2. Heating:
3.2 Thermal cracking experiments

A horizontal furnace including a tube made of 304 stainless steel, with a length of 50 cm, an external diameter of 2.54 cm, and an internal diameter of 2.24 cm the heating unit. The purpose of the stainless steel tube was to hold the sample. The relatively high thermal conductivity reduced the temperature difference between furnace and sample. As Section 3.2.2 mentioned the heating rate was 2°C/min.

3. University of Utah condensation system:

The condensation system of the setup at University of Utah was composed of a modular system where condensable fractions were collected by condensation and absorption in a solvent. The system consisted in 2 modules: a warm vessel with temperature set at 39°C and a cold vessel set at -12°C. Bubblers with isopropanol were located in these modules. Gases passed through bubblers where they were condensed and absorbed into the solvent [72].

4. Gas analysis:

After condensation, non-condensable fractions were analysed in an Agilent 490 micro-GC that used two columns: a CP-Molsieve 5A column with 20 meters and a PPQ (Pora Plot Q) column with 10 meters. The first column analysed the non-organic species such as N₂, O₂ and H₂, whereas the second one studied the organic species such as CH₄, C₂H₆ and C₂H₄. The micro-GC device used a thermal conductivity detector (TCD). Appendix C presents a linear calibration curve of the studied gases and the information of the micro-GC method. Methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄) and hydrogen (H₂) were the non-condensable fractions studied.

3.2.6. Mass balance closure

This study collected condensable gases and analysed non-condensable fractions during the experimental test. It also recovered a solid residue from the reactor after the experimental runs. Once all the fractions were recovered and analysed, this work determined the weight of each fraction. After that, the mass balance closure was calculated by adding each weight and comparing the result of the sum with the weight of the charged sample into the reactor. For this study, the average mass balance closures for crude oil, maltenes, and asphaltene concentrate experiments were 93 %, 97 % and 96 % respectively. Appendix D presents the mass balance closure data.

3.2.7. Confidence intervals of the experimental points

The confidence intervals of the experimental targets were calculated using the Student’s t-distribution for 3 samples (two replica) and a 95 % confidence interval. Appendix E presents the Student’s t-distribution calculations.
3.2.8. Post-experiment analyses

The solid residue was separated into maltenes, asphaltenes and coke. The first two pseudo-components were separated by applying the standard method IP 469, using an IATROSCAN MK-6 equipment. Coke was determined as the insoluble fraction in toluene. In addition to these analyses, elemental and proximate test were carried out on the solid residue to establish the advance in cracking reactions by considering H/C ratio, volatile matter, and fixed carbon content. Condensable fractions were analysed by SIMDIS test, applying ASTM 2887 standardized test using an Agilent 7890A GC, to determine the range of molecular weights for this sample. This sample was also analysed with a GC-MS to characterize components in this sample. Non-condensable fractions were studied using an Agilent 490 micro-GC, the composition and the yield of this sample was found.

3.2.9. TGA experiments

TGA experiments were carried out in a TGA-Q50 thermobalance using the same samples of the horizontal furnace experiments. TGA experiments conditions were: 100 % nitrogen atmosphere, heating rate of 2°C/min up to 450°C and a flow rate of the carrier gas of 100 ml/min.

3.3. Reaction model and determination of kinetic parameters

This study proposed a reaction mechanism that captured the global behavior observed during experiments. Given the complexity of crude, the reaction mechanism was proposed without actual species, but using pseudo-components. The set of differential equations that gave the mass balance of each pseudo-component had the following form:

\[
\frac{dy^k}{dt} = k^j y^k_r
\]

where \( \frac{dy^k}{dt} \) is the change in the yield of the \( i \)th product with time, \( y^k_r \) is the yield of the \( k \)th reactant and \( k^j \) is the reaction rate constant of the \( j \)th reaction. The reaction rate constant was represented by the Arrhenius law:

\[
k^j = k^j_0 e^{-E^j_a/RT}
\]

As this study is related with the thermal decomposition of molecules, then it makes sense to describe the process involving uni-molecular reactions, i.e., first order reactions. It is not considered the interaction between two or more molecules that lead with higher order of reactions. For this reason, the model that described the reaction mechanism supposed an order of reaction of 1. A reaction-controlled
system, i.e., a low Damkhöler number is also supposed. Appendix I presents the reasons for the reaction-controlled system supposition.

Given the set of differential equations that mathematically described the proposed reaction mechanism, the author used an algorithm that applied an unconstrained nonlinear optimization to find the kinetic parameters. This algorithm found the minimum of the objective function defined as sum of square error (SSE), between the experimental and the predicted yields for each pseudo-component, as Equation 3.4 indicates. The regression coefficient was calculated as indicated by Kutner et al. [73], see equations 3.5 to 3.7

\[
SSE = \sum_{i=1}^{n} (Y_{i}^{\text{exp}} - Y_{i}^{\text{pred}})^2
\]  

\[
R^2 = \frac{SSR}{SST}
\]  

\[
SSR = \sum_{i=1}^{n} (Y_{i}^{\text{pred}} - Y_{\text{avg}}^{\text{exp}})^2
\]  

\[
SST = \sum_{i=1}^{n} (Y_{i}^{\text{exp}} - Y_{\text{avg}}^{\text{exp}})^2
\]

where \(n\) is the number of observations, \(Y_{i}^{\text{exp}}\) and \(Y_{i}^{\text{pred}}\) are the experimental and predicted yields for pseudo-component \(i\), respectively, and \(Y_{\text{avg}}^{\text{exp}}\) is the average of the experimental yields.

This study applied the bootstrap method [74] to estimate an uncertainty for the kinetic parameters. The bootstrap method is used when there is some doubt about the adequacy of the regression function and/or the measured data is insufficient for straightforward statistical inferences [73,75,76]. As Kutner et al. [73] indicates, the bootstrap method calls for the selection from the observed sample data of a random sample of size \(n\) with replacement. Sample with replacement implies that the bootstrap sample may contain some duplicate data from the original sample and omit some other data in the original sample. Next the bootstrap method calculates the kinetic parameters from the bootstrap sample. This leads to the first bootstrap-estimated \(k_j^{\star}\) kinetic parameters. This process is repeated a large number of times; each time a bootstrap sample of size \(n\) is selected with replacement from the original sample and the estimated kinetic parameters are obtained from the bootstrap sample. This work applied the bootstrap process 1000 times and obtained an approximate normal distribution for each kinetic parameter, similar to the normal distribution found for one of the optimized parameter and presented in Figure 3.6. After that the confidence interval was calculated as the mean more or less two times the standard deviation (\(\mu \pm 2\sigma\)). Appendix F presents the results of the bootstrap method.
Figure 3.6: Distribution of one of the optimized kinetic parameter using the bootstrap method.
Chapter 4

Results

This study carried out two kind of thermal cracking experiments. Thermogravimetric analysis (TGA), that included thermograms and the first derivative of the variation of weight with time, known as DTG curve, provided a general idea about the behavior of crude oil, maltenes, and asphaltic concentrate during thermal cracking. Cracking experiments in a horizontal furnace allowed to establish the advance of the thermal cracking reactions and characterize cracking products such as: residue, condensable and non-condensable fractions. Sections 4.1 and 4.2 present the TGA and the horizontal tube experimental results respectively, whereas Section 4.3 shows the characterization of the cracking products. Section 4.4 presents a pseudo-mechanism with kinetic parameters that was based on the experimental data.

4.1. TGA experiments

The TGA thermograms, presented in Figure 4.1, give evidence that asphaltenes are the fraction of the crude oil most resistant to thermal degradation. Figure 4.1 shows that the highest weight-loss of the asphaltic concentrate is at temperatures higher than 340°C. Up to this temperature the asphaltic concentrate only lost 10% of its weight. Maltenes also present a significant weight-loss at temperatures higher than 340°C, but at this temperature maltenes had already lost 46% of its weight.
The TGA thermograms are also the source of data for Figure 4.2 that show the DTG curves. DTG curve of the TGA experiments of thermal cracking of crude oil and maltenes presents two peaks, as Figure 4.2 shows. The first peak in the range of temperature from 60°C to 325°C is due to evaporation [47]. The second peak in the DTG curves of crude oil and maltenes, and the last peak for the asphaltenic concentrate give evidence of the cracking reaction. Based on these DTG curves, the cracking reaction takes place in the range between 330°C and 450°C.

The DTG curve of the thermal cracking of the asphaltenic concentrate, presented in Figure 4.2, has a first peak in the range of 90°C and 230°C resulting in the evaporation of the remnant-maltenes in the asphaltenic concentrate sample. This DTG curve presents a second small peak located in the range of 250°C-320°C, indicating the occurrence of reactions at temperatures below those of the thermal cracking. The existence of this reaction regime may be explained by the elimination of groups situated at peripheral sites of the asphaltenes, process that occurs at this range of temperature as indicated by Karacan et al. [38] and suggested by Moschopedis et al. [77].

The maximum of each peak indicates the temperature for the maximum weight loss rate. Table 4.1 presents the temperature at the maximum weight loss rate for evaporation and cracking process. The

![Figure 4.1: TGA thermogram for crude oil, maltenes and asphaltenic concentrate](image)

The TGA thermograms are also the source of data for Figure 4.2 that show the DTG curves. DTG curve of the TGA experiments of thermal cracking of crude oil and maltenes presents two peaks, as Figure 4.2 shows. The first peak in the range of temperature from 60°C to 325°C is due to evaporation [47]. The second peak in the DTG curves of crude oil and maltenes, and the last peak for the asphaltenic concentrate give evidence of the cracking reaction. Based on these DTG curves, the cracking reaction takes place in the range between 330°C and 450°C.

The DTG curve of the thermal cracking of the asphaltenic concentrate, presented in Figure 4.2, has a first peak in the range of 90°C and 230°C resulting in the evaporation of the remnant-maltenes in the asphaltenic concentrate sample. This DTG curve presents a second small peak located in the range of 250°C-320°C, indicating the occurrence of reactions at temperatures below those of the thermal cracking. The existence of this reaction regime may be explained by the elimination of groups situated at peripheral sites of the asphaltenes, process that occurs at this range of temperature as indicated by Karacan et al. [38] and suggested by Moschopedis et al. [77].

The maximum of each peak indicates the temperature for the maximum weight loss rate. Table 4.1 presents the temperature at the maximum weight loss rate for evaporation and cracking process. The
results in Table 4.1 and Figure 4.2 show that the asphaltenic concentrate is the sample that needed the highest temperature to achieve the maximum weight loss-rate (420°C), maltenes was the sample that needed the lowest temperature (400°C), whereas the crude oil requires an intermediate temperature (408°C).

![Figure 4.2: DTG curves for crude oil, maltenes and asphaltenic concentrate](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Evaporation</th>
<th>Cracking</th>
<th>Elimination of peripheral groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DTG (%/°C)</td>
<td>T&lt;sub&gt;max&lt;/sub&gt; (°C)</td>
<td>DTG (%/°C)</td>
</tr>
<tr>
<td>Crude oil</td>
<td>0.033</td>
<td>185</td>
<td>0.39</td>
</tr>
<tr>
<td>Maltenes</td>
<td>0.036</td>
<td>185</td>
<td>0.32</td>
</tr>
<tr>
<td>Asphaltenic concentrate</td>
<td>0.04</td>
<td>174</td>
<td>0.47</td>
</tr>
</tbody>
</table>
4.2. Thermal cracking experiments

According to thermal cracking experiments crude oil, maltenes and asphaltenic concentrate yield mainly two products: a solid residue composed of maltenes, asphaltenes and coke; and volatile products that could be condensable or non-condensable.

Section 4.2.1 presents the results of the thermal cracking of crude oil. These results provide a general idea of the variation of the yield of thermal cracking products with temperature. Sections 4.2.2 and 4.2.3 show the results of the thermal cracking of maltenes and asphaltenic concentrate samples. These experimental results give an explanation about how maltenes and asphaltenes individually react during the thermal cracking process.

4.2.1. Thermal cracking of Castilla crude oil

Thermal cracking of Castilla oil was carried out at two temperatures: 300°C and 450°C. The experiment at 300°C was carried out at Universidad Nacional de Colombia, and the experiment at 450°C was performed at University of Utah. The mass balance of the experiments at University of Utah closed within 93%, as Section 3.2.6 indicated.

These mass balance closure data apply for the experiments at University of Utah where it was possible a more accurate measurement of the condensable and non-condensable fractions than at Universidad Nacional de Colombia. The yield of the solid residue, i.e. the yield of maltenes asphaltenes and coke, was establish at Universidad Nacional de Colombia. To ensure that the experiments at Universidad Nacional and at University of Utah were repeatable, a control point was established at 450°C as Figure 4.3 shows. The non-condensable fractions were measured at University of Utah for all the experimental temperatures because the micro-GC allowed to measure the gases at all the temperatures without stop the run. The condensable fractions (distillables and LMWM) were measured at University of Utah experiment at 450°C and was establish for the experiment at 300°C as the difference between the mass balance closure, the yield of the solid residue and the yield of the non-condensable fraction at 300°C. Figure 4.3 makes the difference between the targets measured at Universidad Nacional de Colombia and the targets established at University of Utah.

Figure 4.3 shows the variation with temperature of the yield of the different products during cracking of Castilla oil. Castilla oil producess 0.38 g/gtot of a condensable fraction at temperatures lower than 300°C. The TGA results discussed in Section 4.1, indicate that this initial weight loss is due to evaporation to which maltenes are exposed (the lighest crude oil fraction) up to 325°C. Based on these results one can concluded that the first step of the thermal cracking process is evaporation. This evaporation process yields a condensable fraction that was called distillables, and a maltene fraction
without distillables that remained in the furnace. This maltene fraction is the one available for the thermal cracking process and was named maltenes*.

After the evaporation process, the initial value for the yield of maltenes* is 0.40 g/gtot, and 0.38 g/gtot for the yield of distillables at 300°C. Asphaltenes also undergo an initial weight loss from 0.19 g/gtot (the initial content of asphaltenes in the crude oil) to 0.14 g/gtot at 300°C. As this initial weight loss proceeds below 300°C, it may be due to elimination of groups located at the peripheral sites of asphaltenes before thermal cracking reactions, as mentioned in Section 4.1. There is no significant presence of coke at 300°C.

As evaporation ends at 325°C, and cracking reactions start at about 330°C, this study suggests that for the experiments carried out at 450°C the condensable fractions recovered at temperatures higher than 330°C are product of the thermal cracking reactions. This condensable fraction was labeled as low-molecular-weight maltenes (LMWM) to make that distinction from the condensables from evaporation. Section 4.3.4 explains why the author selected this name for this condensable fraction. The yield of maltenes* and asphaltenes decrease to 0.23 g/gtot and 0.02 g/gtot respectively at 450°C. Meanwhile the yields of LMWM and coke increase up to 0.29 g/gtot and 0.05 g/gtot respectively. The yield of LMWM was established as the difference between the total yield of condensable fractions and the yield of distillables. The yield of gas is almost negligible during crude oil thermal cracking as it barely reaches a maximum value of $4.73 \times 10^{-3}$ g/gtot at 450°C.

To give more confidence of the experimental results, Figure 4.3 presents as well control points for the experiments ran at University of Utah and Universidad Nacional de Colombia. The yield of the solid residue at 450°C is the same for the experimental runs performed at both universities.
Figure 4.3: Variation of the yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of Castilla crude oil. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure. Error bars for the gas fraction are of the order of the data symbols and are not seen at the scale of the figure. Maltenes*, asphaltenes and coke were measured at Colombia; LMWM, distillables and gas were measured at University of Utah.

Table 4.2 summarizes the average yield of maltenes*, asphaltenes, coke, condensables and gas at each experimental temperature.
Table 4.2: Yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of Castilla crude oil

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (g/gtot)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 (°C)</td>
</tr>
<tr>
<td>Maltenes*</td>
<td>0.81 (±0.01)</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>0.19 (±0.01)</td>
</tr>
<tr>
<td>Coke</td>
<td>0</td>
</tr>
<tr>
<td>Distillables</td>
<td>0</td>
</tr>
<tr>
<td>LMWM</td>
<td>0</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
</tr>
</tbody>
</table>

4.2.2. Thermal cracking of maltenes*

Based on the results of the TGA for maltenes and the thermal cracking of Castilla oil, where maltenes suffered an initial weight loss because of evaporation, this study stated that the first step of the cracking process is evaporation, leaving as products distillables and maltenes without this distillable fraction. To distinguish between the original maltenes and maltenes after evaporation, the latter were identified as maltenes*, that is the fraction available for the cracking process. For this reason this section deals with the thermal cracking of maltenes*.

As with thermal cracking experiments of crude oil (see Section 4.2.1), the yield of maltenes*, asphaltenes and coke were determined with the experiments run at Universidad Nacional de Colombia. Whereas, the yield of volatile products (distillables, LMWM and non-condensables fractions) were established with the experiments run at University of Utah. As Figure 4.4 the control points are located at 300°C and 350°C. The mass balance of the experiments at University of Utah closed within 97%.

Figure 4.4 presents the variation of the yield of the cracking products with temperature during the thermal cracking of maltenes*. Figure 4.4 shows that evaporation produces 0.44 g/gtot of distillables and 0.49 g/gtot of maltenes* at 300°C. The yield of maltenes* decreases from 0.49 g/gtot to 0.40 g/gtot, and the yield of distillables increases up to 0.47 g/gtot from 300°C to 350°C. It is important to highlight that the yield distillables between 300°C and 325°C was estimated as 0.03 g/gtot based on the results obtained from the TGA and described in Section 4.1. Thus, the yield of distillables is 0.44 g/gtot released up to 300°C, plus the 0.03 g/gtot as estimated between 325°C and 350°C. The yield of LMWM at 350°C was estimated as the difference between the total amount of condensable fractions collected at 350°C and the yield of distillables which is equal to 0.02 g/gtot. At 450°C the yield of maltenes* decreases down to 0.11 g/gtot, meanwhile the yield of LMWM achieves a value
as high as 0.29 g/gtot. This value suggests that maltenes* yield mainly LMWM during the cracking process. The yield of asphaltenes becomes significant with a value of 0.07 g/gtot at 400°C. The yield of coke is 0.03 g/gtot at 450°C. These results evidence that maltenes* only produce high-molecular weight species when T>400°C. The yield of gases is very low and increases from $4.81 \times 10^{-4}$ g/gtot to $4.24 \times 10^{-3}$ g/gtot from 300°C to 450°C. As was the case during thermal cracking of crude oil, the yield of gas was very low during the thermal cracking of maltenes*.

The small difference in the yield of the solid residue between the experiments at University of Utah and Universidad Nacional de Colombia is evidence of the repeatability of the experiments. The yield of solid residue were 0.54 g/gtot (Utah) and 0.52 g/gtot (Colombia) at 300°C; and 0.49 g/gtot (Utah) and 0.46 g/gtot (Colombia) at 350°C. Table 4.3 summarizes the average yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas at each experimental temperature. As discussed above, the results include an estimated uncertainty related to a 95% confidence interval. While the table agrees with the results discussed above related to Figure 4.4, it is interesting to note that the uncertainty is very low in most cases. The more evident exceptions are the values for the yield of gas and coke temperatures below 400°C for which that uncertainty is comparable to the measured value. This is explained because of the very low conversion to gas and coke at those temperatures in these experiments.
Figure 4.4: Variation of the yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of maltenes*. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure. Error bars for the gas fraction are of the order of the data symbols and are not seen at the scale of the figure. Maltenes*, asphaltenes and coke were measured at Colombia; LMWM, distillables and gas were measured at University of Utah.
Table 4.3: Yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of maltenes*

<table>
<thead>
<tr>
<th>Product</th>
<th>25 (°C)</th>
<th>300 (°C)</th>
<th>350 (°C)</th>
<th>400 (°C)</th>
<th>450 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maltenes*</td>
<td>1 (±0.01)</td>
<td>0.49 (±0.01)</td>
<td>0.40 (±0.01)</td>
<td>0.26 (±0.01)</td>
<td>0.11 (±0.01)</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>0</td>
<td>0.02 (±0.01)</td>
<td>0.04 (±0.01)</td>
<td>0.07 (±0.01)</td>
<td>0.07 (±0.01)</td>
</tr>
<tr>
<td>Coke</td>
<td>0</td>
<td>0.01 (±0.01)</td>
<td>0.02 (±0.01)</td>
<td>0.01 (±0.01)</td>
<td>0.03 (±0.01)</td>
</tr>
<tr>
<td>Distillables</td>
<td>0</td>
<td>0.44 (±0.03)</td>
<td>0.47 (±0.03)</td>
<td>0.47 (±0.03)</td>
<td>0.47 (±0.03)</td>
</tr>
<tr>
<td>LMWM</td>
<td>0</td>
<td>0 (±0.03)</td>
<td>0.02 (±0.03)</td>
<td>0.15 (±0.03)</td>
<td>0.29 (±0.03)</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
<td>4.81 × 10⁻⁴</td>
<td>5.92 × 10⁻⁴</td>
<td>7.95 × 10⁻⁴</td>
<td>4.1 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(±7.0 × 10⁻⁴)</td>
<td>(±7.0 × 10⁻⁴)</td>
<td>(±7.0 × 10⁻⁴)</td>
<td>(±7.0 × 10⁻⁴)</td>
</tr>
</tbody>
</table>

4.2.3. Thermal cracking of asphaltenic concentrate

Cracking experiments of the asphaltenic concentrate were carried out from 300°C to 450°C. The mass balance for these experiments closed within 96%. The yield of the cracking products (solid residue, distillables and LMWM) were established with experiments performed at Universidad Nacional de Colombia, except for the non-condensable fractions that were studied at University of Utah.

Figure 4.5 shows the variation of the yield of various products with temperature during the thermal cracking of asphaltenic concentrate. Based on the information provided by DTG and TGA analysis (Section 4.1, Figure 4.2), the asphaltenic concentrate sample suffered evaporation up to 230°C which suggests the existence of remanent maltenes, these maltenes probably remained after the asphaltenes separation process. The evaporation process yielded 0.27 g/gtot of maltenes* and 0.20 g/gtot of distillables at 300°C.

According to Figure 4.5, asphaltenes suffer a weight loss from 0.53 g/gtot to 0.46 g/gtot from 25°C to 300°C, producing 0.06 g/gtot of condensable fractions (gtot represents the mass of asphaltenic concentrate charged to the reactor, i.e., the mass of the remanent maltenes-asphaltenes mixture). This weight loss of asphaltenes could be due to the elimination of the peripheral groups, as Section 4.1 suggested. The condensable fractions produced for this process were considered low-molecular-weight maltenes (LMWM), because they are not product of the evaporation process. With this in mind, the yields for cracking of asphaltenic concentrate at 300°C are 0.27 g/gtot for maltenes*; 0.46 g/gtot for asphaltenes; 0.20 g/gtot for distillables and 0.06 g/gtot for LMWM. The yield of LMWM at 300°C was considered only product of the thermal cracking of asphaltenes, because at 300°C maltenes do not produce LMWM as was seen in Figure 4.5; at 300°C maltenes are under evaporation as Figures 4.1
4.2 Thermal cracking experiments

showed.

The yield of asphaltenes decreases from 0.46 g/gtot to 0.37 g/gtot between 300°C and 350°C, i.e., that the yield of asphaltenes decreased 0.09 g/gtot. This decrease in the yield of asphaltenes results in an increase in the yield of maltenes* from 0.26 g/gtot to 0.35 g/gtot. The yield of LMWM does not increase and that of non-condensable fractions in this range of temperature remains below the detection limit. The yield of coke has a slight increment from 0.01 g/gtot to 0.02 g/gtot. As it was seen in Section 4.2.2, during the thermal cracking of maltenes* the yield of maltenes* decreases in the range from 300°C to 350°C, as Figure 4.4 showed. Nevertheless, during the thermal cracking of asphaltenic concentrate the yield of maltenes* increased and, as it was established, at the same rate at which the yield of asphaltenes decreased the yield maltenes* increased. This result suggests that at this range of temperature asphaltenes react yielding maltenes*, which are species of lower molecular weight. The formed maltenes* had boiling points higher than 350°C because were not recovered as condensable fractions.

Between 350°C and 400°C the yield of asphaltenes decreases from 0.37 g/gtot to 0.26 g/gtot, i.e. that the yield decreases 0.11 g/gtot. Meanwhile the yield of maltenes* increases from 0.35 g/gtot to 0.43 g/gtot (the yield increases 0.08 g/gtot); and the yield of LMWM from 0.06 g/gtot to 0.09 g/gtot (the yield increases 0.03 g/gtot). There is no increment in the yield of coke and no presence of non-condensable fractions. As it was mentioned above, according to the results of the thermal cracking of maltenes*, the yield of maltenes* at this range of temperature decreases; nonetheless, with the decreases in the yield of asphaltenes, the yield of maltenes* increased suggesting that asphaltenes yielded maltenes* at this range of temperature. The yield of LMWM increased as the yield of asphaltenes decreased, however, in this case it is not possible to affirm that LMWM only come from the thermal cracking of asphaltenes because, as it was seen in Figure 4.4, maltenes* also yield LMWM at this range of temperature. As in the range from 300°C to 350°C, cracking of asphaltenes yielded species of lower-molecular between 350°C and 400°C.

In the range from 300°C to 400°C the yield of asphaltenes decreased meanwhile the yield of maltenes* and LMWM increased and there was no a significant increment in the yield of coke. These results suggest that asphaltenes decompose to form mainly species of lower-molecular weight such as maltenes* and LMWM in this range of temperature.

The yield of LMWM increases from 0.09 g/got up to 0.18 g/gtot at 450°C; whereas the yield of maltenes* decreases down from 0.43 g/gtot to 0.26 g/gtot which suggests that maltenes* suffer secondary cracking reactions yielding coke precursors and LMWM at temperatures higher than 400°C. This behavior for the maltenes* was already seen during maltenes* thermal cracking experiments as Figure 4.4 showed, where the yield of maltenes* decreased producing LMWM and asphaltenes at
temperatures higher than 400°C. At 400°C the yield of asphaltenes continue decreasing down to 0.18 g/gtot whereas the yield of coke increased from 0.02 g/gtot at 400°C and takes a maximum value of 0.11 g/gtot at 450°C. This fact suggests that asphaltenes yield coke under strong thermal cracking conditions, and after a certain temperature. In this case coke was produced when temperature was higher than 400°C.

![Graph showing variation of yield with temperature](image)

**Figure 4.5:** Variation of the yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of asphaltenic concentrate. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure. Error bars for the gas fraction are of the order of the data symbols and are not seen at the scale of the figure.

Table 4.4 summarizes the average yield of maltenes, asphaltenes, coke, condensables and gas at each experimental temperature with the 95% confidence interval.
4.3 Thermal cracking products

4.3.1 Solid residue

This study considers as solid residue the remaining solid phase after thermal cracking reactions: This solid residue is composed of maltenes, asphaltenes and coke as was explained in the review section. To further characterize this residue, Table 4.5 presents elemental analysis of Castilla crude oil and solid residues recovered after crude oil cracking experiments at 300°C and 450°C. The nitrogen content was estimated at zero for all the experiments. The elemental analysis shows the effect of temperature during thermal cracking process represented in terms of the variation of the H/C atomic ratios. The H/C atomic ratio for Castilla crude oil decreases from 1.34 initially to 1.12 and 0.62 at 300°C and 450°C, respectively. These results indicate that the H/C ratio of the solid residues is lower than the original crude oil sample and that the lowest H/C ratio is for the solid residue recovered at 450°C, the highest experimental temperature. These H/C atomic ratios indicate that during thermal cracking of Castilla crude oil, the H/C ratio of Castilla crude oil decreases with increasing temperature. i.e. that solid residues are more hydrogen deficient than the original crude oil sample, and that this hydrogen deficiency increases with increasing temperature. This last result was confirmed with the analysis of the gaseous phase, presented in Section 4.3.5, with which this study found that yield of hydrogen (H₂) increases with temperature. The hydrogen deficiency could be explain due to cyclization, dehydrogenation and condensation reaction that crude oil undergoes under thermal cracking as authors such as Akmaz et al. [78] indicate.

Table 4.4: Yield of maltenes*, asphaltenes, coke, distillables, LMWM and gas with temperature during thermal cracking of asphaltenic concentrate

<table>
<thead>
<tr>
<th>Product</th>
<th>25 (°C)</th>
<th>300 (°C)</th>
<th>350 (°C)</th>
<th>400 (°C)</th>
<th>450 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maltenes*</td>
<td>0.47 (±0.03)</td>
<td>0.26 (±0.03)</td>
<td>0.35 (±0.03)</td>
<td>0.43 (±0.03)</td>
<td>0.26 (±0.03)</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>0.53</td>
<td>0.46 (±0.03)</td>
<td>0.37 (±0.03)</td>
<td>0.26 (±0.03)</td>
<td>0.18 (±0.03)</td>
</tr>
<tr>
<td>Coke</td>
<td>0</td>
<td>0.01 (±0.03)</td>
<td>0.02 (±0.03)</td>
<td>0.02 (±0.03)</td>
<td>0.11 (±0.03)</td>
</tr>
<tr>
<td>Distillables</td>
<td>0</td>
<td>0.20 (±0.03)</td>
<td>0.20 (±0.03)</td>
<td>0.20 (±0.03)</td>
<td>0.20 (±0.03)</td>
</tr>
<tr>
<td>LMWM</td>
<td>0</td>
<td>0.06 (±0.03)</td>
<td>0.06 (±0.03)</td>
<td>0.09 (±0.03)</td>
<td>0.18 (±0.03)</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0 × 10⁻³</td>
<td>9.2 × 10⁻³</td>
</tr>
</tbody>
</table>

(±1.5 × 10⁻³) (±1.0 × 10⁻³)
Table 4.5: Elemental analysis of crude oil and solid residues recovered at different temperatures

<table>
<thead>
<tr>
<th></th>
<th>Crude oil run up to 300°C</th>
<th>run up to 450 °C</th>
<th>run up to 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%wt.)</td>
<td>87.6</td>
<td>88.2</td>
<td>90.0</td>
</tr>
<tr>
<td>H (%wt.)</td>
<td>9.8</td>
<td>8.3</td>
<td>4.7</td>
</tr>
<tr>
<td>H/C</td>
<td>1.34</td>
<td>1.12</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Figure 4.6 shows a comparison of the H/C atomic ratio of the solid residue with the H/C atomic ratios of other solid fuels. The H/C atomic ratios of Castilla crude oil and the solid residue at 300°C are similar to that of a Canadian asphaltene. This similarity indicates the heavy nature of the crude oil, and that the cracking process up to 300°C has not involved a strong chemical change in the sample compared to the original. The H/C atomic ratio of the solid residue at 450°C, that is the H/C atomic ratio expected for a coke (0.6) according to the literature [14, 25, 27–29], is more hydrogen-deficient than coal indicating. The H/C atomic ratio of the solid residue at 700°C is similar to that of an anthracite, highlighting the hydrogen deficiency of the sample after the thermal process, and the effect of the high temperature in the chemical structure of the original sample. Despite hydrogen deficiency of the solid residue at 700°C, this sample still needs further cracking to have chemical properties, H/C atomic ratio, similar to those of graphite.
Table 4.6 presents the results of the proximate analysis of the fresh crude oil and the solid residues recovered at different temperatures. As expected the volatile matter content of the solid residues decreases with the increase in the cracking temperature. Volatile matter content has not a significant decrease from the initial experimental conditions to 300°C, because evaporation is the only process that takes place at this range of temperature. On the contrary volatile matter has a significant drop from 84.6% to 57.4% and then to 17.5% due to cracking reactions at 300°C, 450°C and 700°C, respectively. The increase in the fixed carbon content with temperature is due to cracking reactions that remove volatile matter leaving more stable or maturated fractions such as asphaltenes and coke. Fixed carbon content is 15.4% at 300°C and achieves a value as high as 82.5% at 700°C.
Table 4.6: Proximate analysis of crude oil and solid residues recovered at different temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Fresh crude oil</th>
<th>300°C</th>
<th>450°C</th>
<th>700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter (%)</td>
<td>88.4</td>
<td>84.6</td>
<td>57.4</td>
<td>17.6</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>11.6</td>
<td>15.4</td>
<td>42.6</td>
<td>82.5</td>
</tr>
</tbody>
</table>

4.3.2. Coke

Figure 4.7 presents the comparison of the variation in the yield of coke with temperature during thermal cracking of crude oil, maltenes* and asphaltenic concentrate.

It is not clear which yield is the highest or the lowest at 300°C. However, observing the experimental targets at 300°C and the error bars, it seems like the yield of coke from thermal cracking of the samples is not significant at this temperature and has about the same value (0.01 g/gtot).

The yield of coke that is product of the cracking of asphaltenic concentrate is higher than the yield of coke resulted from thermal cracking of crude oil and maltenes* at 350°C. There is a rapid increment in the yield of coke originated during cracking of asphaltenic concentrate, from 0.02 g/gtot to 0.11 g/gtot, and coke arised from crude oil cracking (up to 0.05 g/gtot) in the range from 400°C to 450°C. These results suggest that asphaltenes have an important influence in the formation of coke during thermal cracking of crude oil under strong thermal cracking conditions (T>400°C) and that is responsible of most of the coke formatted.
4.3 Thermal cracking products

Figure 4.7: Variation of the yield of coke with temperature during thermal cracking of crude oil, maltenes and asphaltenic concentrate. All the experiments were run at 300°C, 350°C, 400°C and 450°C, nonetheless, the temperatures were displaced to see the error bars in the figure.

4.3.3. Distillables

Section 4.2.1 made a distinction between condensable-fractions product of evaporation (distillables) and condensable-fractions originated during thermal cracking (low-molecular-weight maltenes, LMWM). The current section presents the yield and composition of the distillables that resulted from the evaporation of Castilla oil.

Table 4.7 presents the yield of distillables with temperature during thermal cracking of crude oil, maltenes* and asphaltenic concentrate. Table 4.7 shows that the highest yield of distillables is for those product of the evaporation of maltenes (0.47 g/gtot). This result is expected, considering that maltenes is the fraction of the crude oil that contains the most volatile species. The yield of distillables that resulted from the evaporation of crude oil is 0.38 g/gtot. The asphaltenic concentrate had the
lowest yield of distillables (0.20 g/gtot). This result is because of the low concentration of maltenes in the asphaltene concentrate in comparison with the crude oil and maltenes samples.

**Table 4.7:** Yield of distillables with temperature during thermal cracking of crude oil, maltenes* and asphaltene concentrate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (g/gtot) 300 (°C)</th>
<th>Yield (g/gtot) 350 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>0.38 (±0.03)</td>
<td>0.4 (±0.03)</td>
</tr>
<tr>
<td>Maltenes*</td>
<td>0.44 (±0.04)</td>
<td>0.47 (±0.04)</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>0.2 (±0.03)</td>
<td>0.2 (±0.03)</td>
</tr>
</tbody>
</table>

This study considered that species evolved from any sample at temperatures below 325°C thanks to evaporation. The ASTM D2887 test method (Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, [79]) lists the boiling point of n-paraffins with less than to 18 carbons as less than 325°C. Therefore, it does not seem unreasonable to assume that hydrocarbons with less than 18 carbons would be part of what was called as the distillable fraction. However, as water has boiling point of 100°C, it would also be part of distillables. The content of water in distillables was estimated from the proximate analysis of Castilla that indicated that the content of water is 5% (see Table 3.2). For a yield of distillables at 325°C of 0.38 g/gtot one can estimate the water content in distillables is 13%.

**4.3.4. Low-molecular-weight maltenes (LMWM)**

As sections 4.2.1 and 4.3.3 indicated, low-molecular-weight maltenes (LMWM) represent the condensable fraction product of the thermal cracking reactions. The yield and the results of some analysis performed on this condensable fraction are presented in the current Section.

Figure 4.8 presents the variation of the yield of LMWM with temperature during thermal cracking. For crude oil, maltenes* and asphaltene concentrate the yields to LMWM at 300°C were 0.03 g/gtot, 0 g/gtot and 0.06 g/gtot respectively. Although evaporation took place up to 325°C, crude oil and asphaltene concentrate yielded LMWM at 300°C probably because of the elimination of peripheral groups of asphaltenes, process that occurs before 300°C, as this study indicated before in Sections 4.1 and 4.2.3. Maltenes at temperatures below 300°C evaporate and do not yield LMWM. However, at 350°C the maltenes that did not evaporate (maltenes*) produced 0.02 g/gtot of LMWM. The yield of LMWM from the cracking of maltenes* increased from 0.02 g/gtot to 0.15 g/gtot from 350°C to 400°C, meanwhile the yield of LMWM resulted from the cracking of asphaltene concentrate increased
from 0.06 g/gtot to 0.09 g/gtot in the same temperature range. At 450°C maltenes* yielded 0.29 g/gtot meanwhile asphaltenic concentrate yielded 0.18 g/gtot. For the cracking of asphaltenic it was difficult to establish if LMWM come from cracking of maltenes*, from cracking of asphaltenes or if it was product of both fractions, because asphaltenic concentrate was a maltenes-asphaltenes mixture, as it was indicated in Section 4.2.3.

A sample of condensable fraction recovered during cracking of crude oil up to 450°C was characterize with SIMDIS test and gas chromatography/mass spectroscopy (GC/MS), to establish its chemical composition. According to the result of SIMDIS the heaviest compound of this sample has 28 carbons (C28) which corresponds to molecular weight of 394.8 Da. This value is lower than previous values reported for oil fractions: Chen et al. [26] reported a molecular weight of 947 Da for resins of Athabasca Bitumen (the heaviest molecule inside the maltenes group); Morgan et al. [80] indicated that a small fraction of maltenes from Maya crude oil had a mass of 2000 Da; result of a SIMDIS test performed on

![Diagram](image-url)
Castilla crude oil reported that a final boiling point (FBP) of Castilla is at 720°C, which corresponds to species of 100 carbons, i.e., with a molecular weight of 1404 Da. In the light of these results, and considering that the collected sample is soluble in n-heptane, this study named this fraction: maltenes of low-molecular weight (LMWM).

It is important to highlight that LMWM result from cracking and not from evaporation. Evidence of this is the fact that according to the result of the SIMDIS performed on crude oil, the yield of condensables exclusively produced from an evaporation process would be 0.33 g/gtot at 450°C. The fact that the actual yield of the condensables fraction in Figure 4.8 is 0.69 g/gtot at 450°C confirms the presence of products of cracking reactions.

A qualitatively GC-MS analysis, unfortunately quantitative results were not available, indicated that the heaviest compound in the sample has 31 carbons (C31), very close to SIMDIS result with 28 carbons (C28). The dominant peaks of the gas chromatogram corresponded to normal paraffins, starting with n-decane (C10H22), bp 174°C, to n-hentriacontane (C31H64), bp 458°C. The gas chromatogram also showed the presence of a branched-chain paraffin, 2,6,10,14 tetramethylpentadecane. The presence of each compound reported by the gas chromatogram was verified with the mass spectrum. Appendix G presents the GC/MS spectrograms. Speight [17] presented similar results for the chemical composition of a condensable fraction, the author reported that the condensable fraction collected during thermal cracking experiments of Athabasca bitumen was composed by normal paraffins up to 26 carbons (C26).

### 4.3.5. Gas

The variation of the yield of (methane (CH4), hydrogen (H2), ethylene (C2H4) and ethane (C2H6)) with temperature during thermal cracking of crude oil, maltenes* and asphaltenic concentrate in Figure 4.9 shows that non-condensable fractions start to evolve in the range from 370°C to 400°C. At higher temperatures the yield increases with temperature. The yield of methane and ethane is significantly higher when compared to the other non-condensable fractions. While during cracking of asphaltenic concentrate, methane and ethane have yields between $2 \times 10^{-4}$ g/tot and $1 \times 10^{-3}$ g/gtot the yield of hydrogen and ethylene varies in the range of $1 \times 10^{-5}$ g/gtot to $1.4 \times 10^{-4}$ g/gtot respectively as Figure 4.9 shows.

Among the four gases studied, ethylene starts evolving at the highest temperature, 420°C, but most of them start to evolve around 370°C. This onset of gas evolution around 370°C is in agreement with the increase in the yield of coke at temperatures higher than 400°C (see Figure 4.7). Asphaltenes, the fraction with the highest coke yield (as seen in Figure 4.7), was also that with the highest yield for the non-condensable fraction for temperatures above 400°C. This result suggests that the non-condensable fraction is the result of strong thermal cracking conditions that lead to coke formation. This idea has
been proposed by other authors such as Mazza and Cormack [32] that indicated that the production of volatiles was proportional to that of coke, fact that the authors attributed to their production from the cracking of the asphaltene fraction. Carvajal [81] based on ab initio calculations found that one of the main products during the process of maturation from asphaltenes to coke were non-condensables fractions.

It is important to clarify that the yield that Figure 4.9 shows is a cumulative yield, i.e., that it is not a yield for each temperature but it is the cumulative total yield of each gas at the temperature.

![Figure 4.9: Variation of the cumulative yield of (a) methane (CH\textsubscript{4}), (b) hydrogen(H\textsubscript{2}), (c) ethylene (C\textsubscript{2}H\textsubscript{4}) and (d) ethane (C\textsubscript{2}H\textsubscript{6}) with temperature during thermal cracking of crude oil, maltenes* and asphaltenic concentrate. All the gases start to evolve in the range from 370°C to 400°C except for ethylene that starts at 420°C.](image)

Table 4.8 presents the cumulative yields and the molar composition of the non-condensable fraction for thermal cracking of crude oil, maltenes* and asphaltenic concentrate at 450°C and crude oil at 700°C. The concentration of the gases released during cracking of these samples at 450°C was very low and did
The yields of methane during cracking of crude oil, maltenes* and asphaltene concentrate were $2.4 \times 10^{-3}$, $2.6 \times 10^{-3}$ and $5.6 \times 10^{-3}$ respectively. The mass percentages of methane were 62%, 62% and 61% for cracking of crude oil, maltenes* and asphaltene concentrate, respectively. Comparing the composition of the non-condensable fraction after thermal cracking of crude oil at 450°C and 700°C, there was an increment in the yield of methane from 62% to 75% and an increase in the yield of hydrogen from 2% to 6%. Meanwhile the yields of ethylene and ethane decreased from 5% to 4% and 31% to 15% respectively, this result indicates that production of methane and hydrogen are favored at high temperatures ($T>550°C$).

Figure 4.10 presents the behavior of the cumulative yields of methane, hydrogen, ethylene and ethane with temperature during cracking of crude oil up to 700°C. Only methane and hydrogen were produced up to 700°C. The constant cumulative yield of ethylene and ethane at temperatures higher than 550°C indicates that the formation of these two species ceased at that temperature. Methane and ethane had the highest yields during thermal cracking at 450°C and also at 700°C. While the yield of hydrogen was low in all the temperature range hydrogen was constantly produce, even at temperatures higher than 550°C, where the formation of ethane and ethylene finished. The constant production of hydrogen with temperatures agrees with the fact that the H/C atomic ratio of the solid residue recovered at 700°C was 0.24. This is, hydrogen was available in the sample.

A similar trend was found by Moschopedis et al. [77] during thermal cracking of asphaltenes up to 600°C. The trend of hydrogen suggests that dehydrogenation reactions are stronger at high temperatures, at least over 550°C, and that the presence of this non-condensable fraction at elevated temperatures indicates severe thermal degradation as Moschopedis et al. [77] suggested. Taking into account this last result and the fact that methane was also produced up to 700 °C and has the highest yield among the four non-condensable fractions studied, as it was indicated above, it was concluded that during the formation and maturation of coke, dehydrogenation and demethylation reactions are predominant as indicated by Carvajal [81].
Table 4.8: Yield and composition of gases for cracking of crude oil (CO), maltenes* (M) and asphaltenic concentrate (AC) at 450 °C and crude oil at 700°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>CO (450°C)</th>
<th>M (450°C)</th>
<th>AC (450°C)</th>
<th>CO (700°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y (g/gtot)</td>
<td>%wt.*</td>
<td>%mol.*</td>
<td>Y (g/gtot)</td>
</tr>
<tr>
<td>CH4</td>
<td>2.4 × 10^{-3}</td>
<td>62 (±7 × 10^{-6})</td>
<td>2.6 × 10^{-3}</td>
<td>62 (±4 × 10^{-6})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>8.7 × 10^{-5}</td>
<td>2 (±8 × 10^{-7})</td>
<td>1.1 × 10^{-4}</td>
<td>3 (±3 × 10^{-7})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2H4</td>
<td>1.8 × 10^{-4}</td>
<td>5 (±3 × 10^{-6})</td>
<td>2 × 10^{-4}</td>
<td>5 (±5 × 10^{-6})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2H6</td>
<td>1.2 × 10^{-3}</td>
<td>31 (±9 × 10^{-6})</td>
<td>1.2 × 10^{-3}</td>
<td>30 (±8 × 10^{-6})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>±0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>3.8 × 10^{-3}</td>
<td>100 (±3 × 10^{-4})</td>
<td>4.1 × 10^{-3}</td>
<td>100 (±7 × 10^{-4})</td>
</tr>
</tbody>
</table>

* The mass and the molar percentages were calculated with respect to the total amount of the non-condensable fraction.
Figure 4.10: Variation of the cumulative yield of (a) methane (CH$_4$), (b) hydrogen (H$_2$), (c) ethylene (C$_2$H$_4$) and (d) ethane (C$_2$H$_6$) with temperature during thermal cracking of crude oil up to 700°C. All the gases start to evolve in the range from 370°C to 400°C except for ethylene that starts at 420°C.

### 4.4. Thermal cracking pseudo-mechanism for Castilla crude oil

Based on all the experimental results described above, a reaction pseudo-mechanism for the thermal cracking of crude oil was proposed.

Given the complexity of crude oil, a pseudo-mechanism based on actual chemical species that describe the formation of coke during cracking of oil would be a very difficult ordeal. The alternative taken by the petroleum industry is the use of pseudo-components. A similar approach was taken in this research to improve the chemical understanding of the coke-formation process.
4.4.1. Proposed pseudo-mechanism

As the experimental evidence discussed above showed, the lightest fraction of the crude oil, maltenes, suffered an evaporation process before the onset of thermal cracking reactions. To account for this in the pseudo-mechanism for the cracking of crude oil that this study proposes in Figure 4.11, evaporation yields two fractions of hydrocarbons: (1) Distillables or the hydrocarbons of lower molecular weight that were collected in the condensation system and (2) Maltenes* the hydrocarbons with higher molecular weight that did not evaporate and remained with the sand and become available for the thermal cracking reactions. As the other fractions of oil undergo cracking reactions that yield hydrocarbons of molecular weight similar to maltenes, maltenes* does not only consider the hydrocarbons that did not evaporate, but also those that resulted from the cracking of other oil fractions that were heavy enough and remained in the solid matrix. Thus maltenes* represents the original maltenes without its distillable part and a product of the cracking of asphaltenes. The pseudo-mechanism also distinguishes between the condensable fraction that resulted from evaporation and those product of the cracking reactions. To differentiate all these intermediates and products cracking in the pseudo-mechanism, the condensable fractions that result from evaporation were named distillables those from cracking reactions low-molecular-weight maltenes (LMWM) and the non-condensable fraction as gas. In the pseudo-mechanism in Figure 4.11 maltenes*, during thermal cracking, yield species of lower molecular weight such as LMWM and gas, but also species of higher molecular weight such as asphaltenes that finally lead to coke. A similar process occurs with asphaltenes that yield species of lower molecular weight (maltenes*, LMWM and gas) and species of higher molecular weight, coke.
This pseudo-mechanism considers that coke is only produced by the cracking of asphaltenes; Nonetheless, maltenes* also contribute to the final yield of coke because of the existence of thermal cracking reactions that convert maltenes* into asphaltenes. One important feature of this pseudo-mechanism is that crude oil fractions not only go to heavier fractions but they can lead to species of lower-molecular weight under thermal cracking conditions. For this reason, the pseudo-mechanism considers the formation of low-molecular-weight species from species with higher molecular weight. e.g., the formation of maltenes* from asphaltenes and those of LMWM and gas from maltenes* and asphaltenes.

In contrast to others crude oil cracking models, the one proposed in Figure 4.11 considers evaporation as an initial stage which allows the distinction between the initial fraction of maltenes and the hydrocarbons that remain in the solid matrix after evaporation, that is the fraction available for the thermal cracking, maltenes*. Figure 4.12 presents a comparison of the reactions considered in this work and the reactions that other authors proposed. The pseudo-mechanism is not only unique in the combination of reactions that considers, but also in the formation of LMWM from asphaltenes and gas from maltenes. While the pseudo-mechanism in Figure 4.11 gives a schematic representation of the reactions taking place during the cracking of crude oil at ISC conditions, it does not provide details of the chemical reactions taking place in the system. Section 4.4.3, below, is an attempt to provide such details.
4.4 Thermal cracking pseudo-mechanism for Castilla crude oil

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Maltenes ➔ Asphaltenes</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Maltenes ➔ Coke</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Maltenes ➔ Gas</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Maltenes ➔ LMWM</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Maltenes ➔ Maltenes*</td>
<td>×</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Asphaltenes ➔ Maltenes</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Asphaltenes ➔ Coke</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Asphaltenes ➔ Gas</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Asphaltenes ➔ LMWM</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

**Figure 4.12:** Comparison of the reactions considered in this work and the reactions that some other authors [7–10] proposed

4.4.2. Kinetic analysis

Equations 4.1 to 4.5 are the differential equations that correspond to the reactions in the proposed pseudo-mechanism for thermal cracking of Castilla oil. Section 3.3 above gave a detailed explanation of the origin of this expressions. $k_1$ to $k_7$ are the first-order kinetic constants for each reaction. As this study is related with the thermal decomposition of molecules, then it makes sense to describe the process involving uni-molecular reactions, i.e., first order reactions, a reaction-controlled system is also supposed, i.e, that mass transport effects were not considered.

$$\frac{dy_{mal*}}{dt} = k_4 y_{asp} - (k_1 + k_2 + k_3)y_{mal*}$$

$$\frac{dy_{asp}}{dt} = k_1 y_{mal*} - (k_4 + k_5 + k_6 + k_7)y_{asp}$$

$$\frac{dy_{LMWM}}{dt} = k_2 y_{mal*} + k_7 y_{asp}$$
\[ \frac{dy_{gas}}{dt} = k_3 y_{mal}^* + k_5 y_{asp} \]  
\[ \frac{dy_{coke}}{dt} = k_6 y_{asp} \]

To solve this set of differential equations, it was necessary to determine two kinetic parameters, activation energy \((E_a)\) and frequency factor \((k_0)\). Table 4.9 presents the kinetic parameters with a 95% confidence intervals calculated by applying minimizing the sum of square errors (SSE) between the experimental and calculated yields of each pseudo-component at each experimental temperature and by the Bootstrap method respectively. While the physical interpretation of the value of kinetic parameters, such as those in Table 4.9, is complicated given the rather empirical approach that the use of pseudo-components impose, it is important to note that most parameters, in particular activation energies, have values typical for chemical-controlled processes. Exceptions to this are the activation energies for reactions 4 and 7 that are too low (26.4 kJ/mol) and too high (9760 kJ/mol) respectively. These two reactions involve the decomposition of asphaltenes and are accompanied by very low pre-exponential factors. Despite having these two similarities, it is not clear why these atypical values occur. Future work may focus on reducing the empirical nature of this mechanism.

Figure 4.13 shows a parity plot, with a good agreement \((R^2=0.97)\), between the predicted and experimental yields. Table 4.10 presents the comparison between the experimental and predicted yields at each experimental temperature. Appendix H also shows the comparison between every experiment and the predicted yields. All these results give evidence of a good agreement between model and experiments.
### Table 4.9: Optimized kinetic parameters

<table>
<thead>
<tr>
<th></th>
<th>k_1</th>
<th>k_2</th>
<th>k_3</th>
<th>k_4</th>
<th>k_5</th>
<th>k_6</th>
<th>k_7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ), J/mol</td>
<td>7.05 ( \times ) 1.0^4</td>
<td>8.15 ( \times ) 1.0^4</td>
<td>1.20 ( \times ) 1.0^5</td>
<td>2.65 ( \times ) 1.0^4</td>
<td>2.14 ( \times ) 1.0^5</td>
<td>1.84 ( \times ) 1.0^5</td>
<td>9.67 ( \times ) 1.0^9</td>
</tr>
<tr>
<td>( k_0 ), s(^{-1})</td>
<td>2.55 ( \times ) 1.0^1</td>
<td>6.37 ( \times ) 1.0^2</td>
<td>2.85 ( \times ) 1.0^4</td>
<td>2.45 ( \times ) 1.0^{-2}</td>
<td>1.07 ( \times ) 1.0^{11}</td>
<td>9.85 ( \times ) 1.0^9</td>
<td>9.89 ( \times ) 1.0^{-1}</td>
</tr>
</tbody>
</table>

\( \pm 2.35 \times 10^0 \)  \( \pm 2.07 \times 10^1 \)  \( \pm 2.16 \times 10^3 \)  \( \pm 1.80 \times 10^{-3} \)  \( \pm 7.40 \times 10^9 \)  \( \pm 6.56 \times 10^8 \)  \( \pm 5.98 \times 10^{-2} \)
Figure 4.13: Parity plot of the predicted and experimental yields for thermal cracking of crude oil (CO), maltenes* (M) and asphaltenic concentrate (AC)
### Table 4.10: Experimental and predicted (in parenthesis) yield in g/gtot according to the proposed pseudo-mechanism for pyrolysis of crude oil (CO), maltenes* (M) and asphaltenic concentrate (AC) at the experimental temperatures

<table>
<thead>
<tr>
<th>pseudo-component</th>
<th>Temperature</th>
<th>300°C</th>
<th>350°C</th>
<th>400°C</th>
<th>450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maltenes* (CO)</td>
<td></td>
<td>0.40 (0.40)</td>
<td>–</td>
<td>–</td>
<td>0.23 (0.16)</td>
</tr>
<tr>
<td>Asphaltene (CO)</td>
<td></td>
<td>0.14 (0.14)</td>
<td>–</td>
<td>–</td>
<td>0.02 (0.04)</td>
</tr>
<tr>
<td>Coke (CO)</td>
<td></td>
<td>0.01 (0.01)</td>
<td>–</td>
<td>–</td>
<td>0.05 (0.03)</td>
</tr>
<tr>
<td>LMWM (CO)</td>
<td></td>
<td>0.38 (0.38)</td>
<td>–</td>
<td>–</td>
<td>0.69 (0.65)</td>
</tr>
<tr>
<td>Gas (CO)</td>
<td></td>
<td>0 (0)</td>
<td>–</td>
<td>–</td>
<td>4.73 × 10⁻³ (7.90 × 10⁻³)</td>
</tr>
<tr>
<td>Maltenes* (M)</td>
<td></td>
<td>0.48 (0.47)</td>
<td>0.41 (0.43)</td>
<td>0.26 (0.31)</td>
<td>0.11 (0.13)</td>
</tr>
<tr>
<td>Asphaltenes (M)</td>
<td></td>
<td>0.023 (0.022)</td>
<td>0.04 (0.03)</td>
<td>0.07 (0.06)</td>
<td>0.07 (0.1)</td>
</tr>
<tr>
<td>LMWM (M)</td>
<td></td>
<td>0 (0)</td>
<td>0.01 (0.03)</td>
<td>0.13 (0.11)</td>
<td>0.27 (0.26)</td>
</tr>
<tr>
<td>Gas (M)</td>
<td></td>
<td>1.51 × 10⁻⁴ (8.10 × 10⁻⁵)</td>
<td>1.51 × 10⁻⁴ (2.70 × 10⁻⁴)</td>
<td>5.67 × 10⁻⁴ (1.33 × 10⁻³)</td>
<td>4.24 × 10⁻³ (4.37 × 10⁻³)</td>
</tr>
<tr>
<td>Maltenes* (AC)</td>
<td></td>
<td>0.28 (0.28)</td>
<td>0.35 (0.38)</td>
<td>0.43 (0.38)</td>
<td>0.26 (0.21)</td>
</tr>
<tr>
<td>Asphaltenes (AC)</td>
<td></td>
<td>0.47 (0.46)</td>
<td>0.37 (0.34)</td>
<td>0.26 (0.22)</td>
<td>0.18 (0.07)</td>
</tr>
<tr>
<td>Coke (AC)</td>
<td></td>
<td>0.008 (0.01)</td>
<td>0.02 (0.01)</td>
<td>0.02 (0.03)</td>
<td>0.11 (0.13)</td>
</tr>
<tr>
<td>LMWM (AC)</td>
<td></td>
<td>0.03 (0.02)</td>
<td>0.06 (0.04)</td>
<td>0.09 (0.13)</td>
<td>0.18 (0.32)</td>
</tr>
<tr>
<td>Gas (AC)</td>
<td></td>
<td>2.89 × 10⁻⁴ (2.80 × 10⁻⁴)</td>
<td>3.22 × 10⁻⁴ (3.40 × 10⁻⁴)</td>
<td>1.35 × 10⁻³ (1.27 × 10⁻³)</td>
<td>8.22 × 10⁻³ (7.95 × 10⁻³)</td>
</tr>
</tbody>
</table>

In addition to the reaction kinetic constants, the evaporation constant was found by minimizing the sum square error (SSE) between the experimental data and calculated yield according to Equation 4.6. Experimental data from TGA thermogram of maltenes cracking at temperatures below 325°C were used. The optimal value for the evaporation constant was 7.5 × 10⁻⁵ (J/mol). Appendix H shows very good agreement between the predicted and the experimental yield of maltenes with temperature during evaporation.

\[
\frac{dy_{mal}}{dt} = -k_e y_{mal}
\]  

(4.6)
4.4.3. Chemistry of the thermal cracking process

This section proposes a chemical explanation for the experimental results presented in this document. This chemical explanation is based on the reaction pathways that Carvajal [81] proposed for the thermal cracking of a crude oil.

The experimental data suggest that both high- and low-molecular-weight molecules (maltenes and asphaltenes) undergo thermal cracking and form radicals. Reaction between these radicals produces low-molecular-weight molecules that can be condensable and non-condensable. Addition of these radicals to high-molecular-weight molecules, promotes growth and eventually, through a series of reactions such as cyclization and aromatization a coke precursor is formed. This coke precursor maturates by becoming more unsaturated and finally lead to coke.

Carvajal [81] determined all possible reactions that hydrocarbons could suffer under thermal cracking conditions typical of ISC. These reactions could be unimolecular (C-C and C-H cleavages), bimolecular initiations, intramolecular and intermolecular H-transfer, β-scission, isomerization, intramolecular and intermolecular addition, cyclization, dehydrogenation and condensation. Carvajal [81] proposed chemical pathways that involved the formation of new species because of growing or breaking of carbon chains.

Figure 4.14 presents a reaction pathway for the cracking of asphaltenes that was shortened from the pathway proposed by Carvajal [81]. Carvajal established that during cracking of asphaltenes the alkyl chains located at peripheral sites of the asphaltene structures are the first portion of asphaltenes that are lost. This first step for the cracking of asphaltenes could be an explanation for the initial weight lost of asphaltenes and the production of LMWM below 300°C. After this first step, the archipelago molecule of asphaltenes is breaked forming independent islands with a simplified structure. This step could be an explanation for the increment in the yield of maltenes*. These first two steps are presented in Figures 4.14a and 4.14b, where it is illustrated the initial lost of alkyl chains and the break of the asphaltene archipelago forming independent islands. The independent structures (islands) suffer a process of maturation where the remaining alkyl chains are removed due to β-scission and C-C cleavage reactions leaving a species as the one presented in Figure 4.14c. The removed alkyl chains could be the reason for the increment in the yield of LMWM during cracking of asphaltene concentrate. During the remove of these alkyl chains, the most stable carbon of the chain remains in the structure, i.e., that only methyl groups remain in the island as presented in Figure 4.14c. After that, the remained methyl groups located at peripheral sites are removed from the structure forming light species such as methanes or ethanes (see Figure 4.14d). This last step could be an explanation for the high yield of non-condensable fractions during cracking of asphaltene, whereas the yield of coke increases. In
this last step Carvajal suggested that non-condensable fractions are composed mainly of methane (CH₄) and ethane (C₂H₆). This suggestion matches with the experimental results where the main non-condensable fraction species were methane and ethane as presented in Section 4.3.5. Figure 4.14 also presents the H/C atomic ratio of each structure. The H/C ratio decreases with the increment in the degree of maturation of the islands due to the elimination of the alkyl chains, this agrees with the experimental results presented above in Section 4.3.1 where H/C ratio of the solid residues are lower than the original crude oil samples after thermal cracking.

Figure 4.14: Summarized reaction pathway for the thermal cracking of asphaltenes and H/C atomic ratio for each step
Chapter 5

Conclusions and recommendations

5.1. Conclusions

TGA thermograms and DTG curves provided a general idea about the behavior of crude oil, maltenes and asphaltenic concentrate under thermal cracking conditions relevant for ISC at atmospheric pressure. Results of these experiments indicated that when Castilla crude oil or its fractions undergoes heating under inert atmosphere at conditions relevant for cracking two in-series processes take place: evaporation of the most volatile fractions between 60°C and 325°C and cracking reactions that mostly start when the temperature is higher than 325°C. According to the thermal cracking experiments carried out in a horizontal tube furnace, the evaporation stage leaves as products a condensable fraction, named distillables that had at maximum 18 carbons and a fraction that did not evaporate and remained in the solid matrix that was named maltenes*. During the cracking stage crude oil, maltenes and asphaltenic concentrate yield two products: a solid residue that was composed of maltenes, asphaltenes and coke and volatile products that could be condensable or non-condensable.

DTG curves showed a mass loss of the asphaltenic concentrate from 250°C to 320°C different to the mass loss due to evaporation. Evidence of loss of asphaltenes below 320°C was also evident during the horizontal tube experiments for the thermal cracking of crude oil and for the asphaltenic concentrate. According to other studies [38, 77, 81] that have registered the same behavior, this initial weight loss of asphaltenes could be due to the elimination of the alkyl chains located at the peripheral sites of the asphaltenes.

The condensable fraction recovered during cracking of crude oil, maltenes and asphaltenic concentrate at temperatures higher than 325°C was product of thermal cracking reactions. This pseudo-component
was named low-molecular-weight maltenes (LMWM), because the results of SIMDIS and the GC-MS qualitative analysis indicated that this sample was composed mainly of n-paraffines with a maximum 28 carbons, i.e., species with a maximum molecular weight of 395 Da, that are much lighter than the fresh maltenes that could have molecular weight as high as 947 Da \[80\]. The yield of LMWM during cracking of crude oil was 0.28 g/gtot. The yield and the composition of this pseudo-component are evidence of the upgrading of the crude oil during the cracking process.

Elemental and proximate analyses of the solid residue recovered after cracking of crude oil gave an insight into the cracking process showing the effect of temperature during cracking reactions. The composition of the residue remains almost constant up to 300°C as up to this temperature the main process is evaporation. The H/C atomic ratio and the volatile matter content did not show a significant decrease from the initial conditions up to 300°C. H/C atomic ratio decreased from 1.34 to 1.12 at 300°C, whereas volatile matter content decreased from 88.4% to 84.6%. The effect was very evident when the temperature was higher than 300°C, particularly higher than 325°C where the cracking process is expected to start. The H/C atomic ratio decreased to 0.62 and the volatile matter to 57.4% at 450°C. The reduction in the concentration of hydrogen with the increase of temperature could be explained by cyclization, dehydrogenation and condensation reactions that crude oil suffers under thermal cracking. The increase of H\(_2\) production with temperature agrees with the reduction on the hydrogen content of the solid matrix. The increase in the fixed carbon content with temperature confirmed that more stable or maturated species such as asphaltenes or coke are products of the thermal cracking reactions. Fixed carbon content was 15.4% at 300°C and achieved a value as high as 82.5% at 700°C.

The significant decrease in the concentration of crude oil, maltenes* and asphaltenes, and with that the formation of lighter and heavier species, such as LMWM and coke at temperatures higher than 400°C, indicates that these species suffer strong thermal degradation and that the cracking products are heavier and lighter species than the original molecules. As a result of this thermal degradation, coke and non-condensable fractions are formed at temperatures higher than 400°C. Asphaltenes are the species that yield the highest quantity of coke with 0.11 g/gtot and the highest amount of non-condensables at the same temperature. Coke and non-condensable fractions formation were proportional and had a strong presence during the cracking of asphaltenes. Methane and ethane were the species with the highest concentration that composed the non-condensable fraction, representing the 62% and 31% mass percentage, respectively, of the total gas production. Methane (CH\(_4\)) and hydrogen (H\(_2\)) were the only gases formed at temperatures higher than 550°C. This result indicates that demethylation
and dehydrogenation reactions are favored under strong cracking conditions and are representative reactions of the maturation of coke as Carvajal [81] indicated.

The proposed pseudo-mechanism captures the results found during the experiments. It considers an initial stage of evaporation that leaves as products distillables and hydrocarbons that did not evaporate and remained in the solid matrix available for the cracking process. During cracking each pseudo-component may yield species of lower and higher molecular weight by different chemical processes. The mechanism also considers the formation of a pseudo-component, LMWM, that resulted from the cracking of maltenes* and asphaltenes and was collected in the condensation system. LMWM is an upgraded species composed mainly of paraffines that have maximum 28 carbons. The pseudo-mechanism considers that coke is the result of the cracking of asphaltenes; nonetheless, maltenes* also contributed to the final yield of coke as this fraction undergoes thermal cracking reactions that yield asphaltenes.

Kinetic parameters were adjusted by minimizing the sum of square error (SSE) between the experimental and calculated yields of each pseudo-component to provide an insight into the thermal cracking of Castilla oil, maltenes* and asphaltenes. A good coefficient of determination was obtained ($R^2=0.97$) and the reactions were well fitted using first order kinetic parameters.

5.2. Recommendations

1. Nuclear Magnetic Resonance (NMR) on the solid residues recovered after thermal cracking of asphaltenic concentrate experiments to confirm the results of this thesis that indicates the elimination of the groups situated at the peripheral sites of asphaltenes.

2. In order to have more realistic results on coke formation, future studies should consider the effect of pressure on the cracking process as oil reservoirs operate above atmospheric pressure.
References


REFERENCES


REFERENCES


Appendix A

Calculation of the residence time

To calculate the time required by the nitrogen flow to cross the reactive zone, i.e. residence time, this study used equations A.1 to A.3

\[ t_r = \frac{L}{V_{N_2}} \]  

(A.1)

where \( t_r \) (s) is the residence time, \( L \) (cm) is the length of the sample inside the sample carrier and \( V_{N_2} \) (cm/min) is the velocity of nitrogen.

The velocity of nitrogen was calculated as:

\[ V_{N_2} = \frac{F_{T_2}}{A} \]  

(A.2)

where \( F_{T_2} \) (cm\(^3\)/min) is the flow of nitrogen at the temperature of the reactive region, \( T_2 \) varied from 300\(^\circ\)C to 450\(^\circ\)C.

\[ F_{T_2} = \frac{F_{T_1} \times T_2}{T_1} \]  

(A.3)

where \( F_{T_1} \) (cm\(^3\)/min) is the flow of nitrogen at the entrance of the reactor which is at ambient temperature (about 25\(^\circ\)C).
Appendix B

Calculation of the Peclet number

Peclet number was calculated using Equation B.1

\[ P_e = \frac{L \times U}{D} \]  

(B.1)

where \( L \) (cm) is the space through which the gases crossed, for this case, it is the internal diameter of the horizontal tube (2.24 cm), \( U \) (cm/s) is the output velocity of the gas at atmospheric pressure and at the maximum temperature of the test. The out velocity was calculated using Equation A.2. \( D \) (\( cm^2/s \)) is the diffusivity of oxygen (O\(_2\)) in nitrogen (N\(_2\)), \( D \) was calculated using Equation B.2 [13].

\[
\frac{pD_{AB}}{(p_{cA}p_{cB})^{1/3}(T_{cA}T_{cB})^{5/12}(1/M_A + 1/M_B)^{1/2}} = a \left( \frac{T}{\sqrt{T_{cA}T_{cB}}} \right)^b
\]

(B.2)

Table B.1 presents the values used for the calculation of the diffusivity of oxygen in nitrogen.

Table B.1: Constants for the calculation of the Diffusivity of oxygen (O\(_2\)) in nitrogen (N\(_2\)) [13]

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.75\times10^{-4}</td>
</tr>
<tr>
<td>b</td>
<td>1.82</td>
</tr>
<tr>
<td>( P_c ) N(_2) (atm)</td>
<td>33.5</td>
</tr>
<tr>
<td>( P_c ) O(_2) (atm)</td>
<td>49.7</td>
</tr>
<tr>
<td>( T_c ) N(_2) (K)</td>
<td>126.2</td>
</tr>
<tr>
<td>( T_c ) O(_2) (K)</td>
<td>154.4</td>
</tr>
<tr>
<td>( M ) N(_2) (g/mol)</td>
<td>28.013</td>
</tr>
<tr>
<td>( M ) O(_2) (g/mol)</td>
<td>31.999</td>
</tr>
</tbody>
</table>
Appendix C

Micro-GC calibration and measurement methodology

Figure C.1 presents the linear calibration curve of the studied non-condensable gases: methane (CH$_4$), ethane (C$_2$H$_6$), ethylene (C$_2$H$_4$) and hydrogen (H$_2$). Table C.1 presents the information of the micro-GC method.
Table C.1: Micro-GC method

<table>
<thead>
<tr>
<th>information</th>
<th>Channel 1</th>
<th>Channel 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured gases</td>
<td>N₂ and H₂</td>
<td>CH₄, C₂H₄ and C₂H₆</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Argon</td>
<td>Helium</td>
</tr>
<tr>
<td>Column description</td>
<td>20m MS5A</td>
<td>10m PPQ</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>110°C</td>
<td>110°C</td>
</tr>
<tr>
<td>Injection time</td>
<td>40 ms</td>
<td>40 ms</td>
</tr>
<tr>
<td>Backflush time</td>
<td>8 s</td>
<td>8 s</td>
</tr>
<tr>
<td>Column temperature</td>
<td>130°C</td>
<td>70°C</td>
</tr>
<tr>
<td>Pressure mode</td>
<td>static</td>
<td>static</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>276 kPa</td>
<td>172 kPa</td>
</tr>
<tr>
<td>Detector sensitivity</td>
<td>extra high</td>
<td>auto</td>
</tr>
<tr>
<td>Run time</td>
<td>140 s</td>
<td>40 s</td>
</tr>
</tbody>
</table>
Appendix D

Mass balance closure

The mass balance closure was obtained by running the thermal cracking experiment using the setup of the University of Utah with crude oil, maltenes and asphaltenes at a heating rate of 2°C/min up to 450°C, once the desired temperature was achieved the experiment was run for 30 minutes more at isothermal condition. This experiment had from 4 to 5 repetitions. Figure D.1 and Table D.1 present the yield of the solid, condensable and gas products after these thermal cracking experiments.

Figure D.1: Yield of thermal cracking products for the mass balance closure experiment
Table D.1: Yield of thermal cracking products for the mass balance closure experiment with a 95% confidence interval

<table>
<thead>
<tr>
<th></th>
<th>Crude oil</th>
<th>Maltenes*</th>
<th>Asphaltenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid product (g/g tot)</td>
<td>$0.16(\pm2.89 \times 10^{-3})$</td>
<td>$0.15(\pm0.02)$</td>
<td>$0.53(\pm0.05)$</td>
</tr>
<tr>
<td>Condensables (g/g tot)</td>
<td>$0.76(\pm0.06)$</td>
<td>$0.81(\pm0.04)$</td>
<td>$0.41(\pm0.01)$</td>
</tr>
<tr>
<td>Gas (g/g tot)</td>
<td>$8.3 \times 10^{-3}$</td>
<td>$6.52 \times 10^{-3}$</td>
<td>$2.05 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$(\pm1.73 \times 10^{-3})$</td>
<td>$(\pm1.73 \times 10^{-3})$</td>
<td>$(\pm2.16 \times 10^{-3})$</td>
</tr>
<tr>
<td>Mass balance closure (%)</td>
<td>93</td>
<td>97</td>
<td>96</td>
</tr>
</tbody>
</table>
Appendix E

Student’s t-distribution calculations

The confidence intervals of the experimental data were calculated using the Student’s t-distribution, that is used to estimate parameters when the sample size is small as it was the case of this study that had 3 samples (two replica). The confidence intervals were calculated applying Equation E.1.

\[
\mu = \bar{x} \pm t \frac{s}{\sqrt{n}}
\]  

(E.1)

where \(\bar{x}\) is the average value, \(s\) is the standard deviation, \(n\) is the number of samples and \(t\) is the student’s T that was taken from Table E.1 for a \(n-1\) degrees of freedom and a confidence level of 95%.

<table>
<thead>
<tr>
<th>ν</th>
<th>Cumulative probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75 0.90 0.95 0.975 0.99 0.995</td>
</tr>
<tr>
<td>2</td>
<td>1.000 3.078 6.314 12.706 31.821 63.657</td>
</tr>
<tr>
<td>3</td>
<td>0.816 1.886 2.922 4.303 6.965 9.925</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>120</td>
<td>0.677 1.289 1.658 1.980 2.358 2.617</td>
</tr>
<tr>
<td>∞</td>
<td>0.674 1.282 1.645 1.960 2.326 2.576</td>
</tr>
</tbody>
</table>

Table E.1: Table of Student t-distribution

In this case for a confidence level of 95%, 2 samples and 1 degree of freedom the Student’s T was 6.3.
Appendix F

Results of the bootstrap method

Figures F.1 to F.4 present histogram plots of the optimized values for each kinetic parameter with
the number of iterations that found that values. These figures allow to visualize that the distribution
of each kinetic parameter is approximately a normal distribution. Figures F.5 and F.6 present scatter
plots for each pair of activation energy and pre-exponential factor.

Figure F.1: Distribution of activation energies for maltenes* reactions
Figure F.2: Distribution of activation energies for asphaltenes reactions
Figure F.3: Distribution of pre-exponential factors for maltenes* reactions
Figure F.4: Distribution of pre-exponential factors for asphaltenes reactions
Figure F.5: Scatter plot of maltenes* kinetic parameters
Figure F.6: Scatter plot of asphaltenes kinetic parameters
Appendix G

Chemical composition of LMWM
(GC/MS report)

This appendix presents the chromatogram and the mass spectra that the GC/MS equipment reported after the analysis of the condensable fraction. In the chromatogram the most predominant peaks correspond to n-paraffines between 10 and 31 carbons (C10 to C31). The mass spectra confirm that the species are n-paraffins and show the presence of a branched-chain paraffin (2,6,10,14 tetramethylpentadecane).
Sample Information

Analyzed by: Admin
Analyzed: 2/26/2015 5:58:42 PM
Sample Type: Unknown
Level #: 1
Sample Name: Crudo 700
Sample ID: Crudo 700
IS Amount: [1]=1
Sample Amount: 1
Dilution Factor: 1
Vial #: 14
Injection Volume: 0.70
Data File: C:\GCMSolution\Lab_Instruments_MS\datos\SERVICIOS_JAPON\300115\Crudo 700_Crudo 700_2262015_6.qgd
Org Data File: C:\GCMSolution\Datos\Quirema\NataliaP\Datos\Crudo 700_Crudo 700_2262015_6.qgd
Method File: C:\GCMSolution\Lab_Instruments_MS\metodos\SERVICIOS_JAPON.qgm
Org Method File: C:\GCMSolution\Lab_Instruments_MS\metodos\SERVICIOS_JAPON.qgm
Report File: 
Tuning File: C:\GCMSolution\System\Tune1\Tuning enero3-2014.qgt
Modified by: Admin
Modified: 4/7/2015 3:17:34 PM

Method

===== Analytical Line 1 =====
$If$(AOC-20i+s!=)
[ AOC-20i+s ]
# of Rinses with Presolvent: 3
# of Rinses with Solvent(post): 3
$If$(3!=)# of Rinses with Sample: 3

[GC-2010]
Column Oven Temp.: 100.0 °C
Injection Temp.: 310.00 °C
Injection Mode: Split
Flow Control Mode: Pressure
Pressure: 16.3 psi
Total Flow: 94.7 mL/min
Column Flow: 1.50 mL/min
Linear Velocity: 45.6 cm/sec
Purge Flow: 3.0 mL/min
Split Ratio: 60.0
Oven Temp. Program

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Hold Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>4.00</td>
</tr>
<tr>
<td>310.0</td>
<td>6.00</td>
</tr>
</tbody>
</table>

[GCMS-QP2010 Ultra]
IonSourceTemp: 250.00 °C
Interface Temp.: 310.00 °C
Solvent Cut Time: 1.60 min
Detector Gain Mode: Relative
Detector Gain: 0.95 kV +0.00 kV
Threshold: 0

[MS Table]
--Group 1 - Event 1--
Start Time: 1.61 min
End Time: 52.00 min
ACQ Mode: Scan
Event Time: 0.30 sec
Scan Speed: 3333
Start m/z: 35.00
End m/z: 1000.00
Sample Inlet Unit: GC
[MS Program]
Use MS Program: OFF
<table>
<thead>
<tr>
<th>Peak#</th>
<th>R.Time</th>
<th>I.Time</th>
<th>F.Time</th>
<th>Area</th>
<th>Area%</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.653</td>
<td>1.620</td>
<td>1.685</td>
<td>33987611</td>
<td>82.73</td>
<td>Octane</td>
</tr>
<tr>
<td>2</td>
<td>2.905</td>
<td>2.870</td>
<td>2.930</td>
<td>121504</td>
<td>0.30</td>
<td>C10</td>
</tr>
<tr>
<td>3</td>
<td>4.438</td>
<td>4.395</td>
<td>4.485</td>
<td>258781</td>
<td>0.63</td>
<td>C11</td>
</tr>
<tr>
<td>4</td>
<td>6.693</td>
<td>6.645</td>
<td>6.750</td>
<td>329593</td>
<td>0.80</td>
<td>C12</td>
</tr>
<tr>
<td>5</td>
<td>9.301</td>
<td>9.225</td>
<td>9.360</td>
<td>557411</td>
<td>1.36</td>
<td>C13</td>
</tr>
<tr>
<td>6</td>
<td>11.982</td>
<td>11.935</td>
<td>12.055</td>
<td>463025</td>
<td>1.13</td>
<td>C14</td>
</tr>
<tr>
<td>7</td>
<td>14.587</td>
<td>14.520</td>
<td>14.660</td>
<td>429295</td>
<td>1.04</td>
<td>C15</td>
</tr>
<tr>
<td>8</td>
<td>17.074</td>
<td>17.025</td>
<td>17.200</td>
<td>768906</td>
<td>1.87</td>
<td>C16</td>
</tr>
<tr>
<td>9</td>
<td>19.431</td>
<td>19.375</td>
<td>19.495</td>
<td>371444</td>
<td>0.90</td>
<td>C17</td>
</tr>
<tr>
<td>10</td>
<td>19.568</td>
<td>19.510</td>
<td>19.645</td>
<td>325386</td>
<td>0.79</td>
<td>2,6,10,14-tetrametilpentadecano</td>
</tr>
<tr>
<td>11</td>
<td>21.673</td>
<td>21.605</td>
<td>21.750</td>
<td>359129</td>
<td>0.87</td>
<td>C18</td>
</tr>
<tr>
<td>12</td>
<td>23.801</td>
<td>23.750</td>
<td>23.895</td>
<td>346685</td>
<td>0.84</td>
<td>C19</td>
</tr>
<tr>
<td>13</td>
<td>25.833</td>
<td>25.775</td>
<td>25.895</td>
<td>323903</td>
<td>0.79</td>
<td>C20</td>
</tr>
<tr>
<td>14</td>
<td>27.773</td>
<td>27.720</td>
<td>27.845</td>
<td>318508</td>
<td>0.78</td>
<td>C21</td>
</tr>
<tr>
<td>15</td>
<td>29.632</td>
<td>29.575</td>
<td>29.715</td>
<td>360125</td>
<td>0.88</td>
<td>C22</td>
</tr>
<tr>
<td>16</td>
<td>31.410</td>
<td>31.360</td>
<td>31.465</td>
<td>303750</td>
<td>0.74</td>
<td>C23</td>
</tr>
<tr>
<td>17</td>
<td>33.120</td>
<td>33.065</td>
<td>33.195</td>
<td>355817</td>
<td>0.87</td>
<td>C24</td>
</tr>
<tr>
<td>18</td>
<td>34.764</td>
<td>34.715</td>
<td>34.855</td>
<td>274361</td>
<td>0.67</td>
<td>C25</td>
</tr>
<tr>
<td>19</td>
<td>36.343</td>
<td>36.290</td>
<td>36.430</td>
<td>245003</td>
<td>0.60</td>
<td>C26</td>
</tr>
<tr>
<td>20</td>
<td>37.864</td>
<td>37.805</td>
<td>37.945</td>
<td>236059</td>
<td>0.57</td>
<td>C27</td>
</tr>
<tr>
<td>21</td>
<td>39.338</td>
<td>39.280</td>
<td>39.395</td>
<td>169241</td>
<td>0.41</td>
<td>C28</td>
</tr>
<tr>
<td>22</td>
<td>40.755</td>
<td>40.710</td>
<td>40.820</td>
<td>177791</td>
<td>0.43</td>
<td>C29</td>
</tr>
</tbody>
</table>

Peak Report TIC

Total Area: 41083328

Percentage: 100.00%
Spectrum
Peak#:4   R.Time:6.693(Scan#:1018)
MassPeaks:517
RawMode:Averaged 6.690-6.700(1017-1019)
BG Mode:Calc. from Peak Group 1 - Event 1

Spectrum
Peak#:5   R.Time:9.301(Scan#:1539)
MassPeaks:543
RawMode:Averaged 9.295-9.305(1538-1540)
BG Mode:Calc. from Peak Group 1 - Event 1

Spectrum
Peak#:6   R.Time:11.982(Scan#:2075)
MassPeaks:483
RawMode:Averaged 11.975-11.985(2074-2076)
BG Mode:Calc. from Peak Group 1 - Event 1
Spectrum

Peak#: 7   R.Time: 14.587(Scan#: 2596)
MassPeaks: 532
RawMode: Averaged 14.580-14.590(2595-2597)
BG Mode: Calc. from Peak Group 1 - Event 1

Peak#: 8   R.Time: 17.074(Scan#: 3094)
MassPeaks: 534
RawMode: Averaged 17.070-17.080(3093-3095)
BG Mode: Calc. from Peak Group 1 - Event 1

Peak#: 9   R.Time: 19.431(Scan#: 3565)
MassPeaks: 493
BG Mode: Calc. from Peak Group 1 - Event 1
Peaks:

Peak#13  R.Time: 25.833 (Scan#: 4846)
MassPeaks: 542
RawMode: Averaged 25.830-25.840 (4845-4847)
BG Mode: Calc. from Peak Group 1 - Event 1

Peak#14  R.Time: 27.773 (Scan#: 5234)
MassPeaks: 457
RawMode: Averaged 27.770-27.780 (5233-5235)
BG Mode: Calc. from Peak Group 1 - Event 1

Peak#15  R.Time: 29.632 (Scan#: 5605)
MassPeaks: 548
RawMode: Averaged 29.625-29.635 (5604-5606)
BG Mode: Calc. from Peak Group 1 - Event 1
Peak# 19: R.Time: 36.343 (Scan#: 6948)
MassPeaks: 505
RawMode: Averaged 36.340-36.350 (6947-6949)
BG Mode: Calc. from Peak Group 1 - Event 1

Peak# 20: R.Time: 37.864 (Scan#: 7252)
MassPeaks: 449
RawMode: Averaged 37.860-37.870 (7251-7253)
BG Mode: Calc. from Peak Group 1 - Event 1

Peak# 21: R.Time: 39.338 (Scan#: 7547)
MassPeaks: 547
RawMode: Averaged 39.335-39.345 (7546-7548)
BG Mode: Calc. from Peak Group 1 - Event 1
Peak #: 22  R. Time: 40.755 (Scan #: 7830)
MassPeaks: 486
Raw Mode: Averaged 40.750-40.760 (7829-7831)
BG Mode: Calc. from Peak  Group 1 - Event 1
Appendix H

Comparison between the experimental and predicted yields

Figures H.1 to H.4 present the comparison between the experimental and the predicted yields for thermal cracking of crude oil, maltenes*, asphaltenes and evaporation of maltenes. In most of cases the predicted values agree with the experimental targets.

- Crude oil thermal cracking

![Graphs showing the comparison between experimental and predicted yields](image)

**Figure** H.1: Experimental and predicted yields for crude oil thermal cracking
Maltenes* thermal cracking

Figure H.2: Experimental and predicted yields for maltenes* thermal cracking
- Asphaltenes thermal cracking

Figure H.3: Experimental and predicted yields for asphaltenes thermal cracking
Evaporation of maltenes

Figure H.4: Experimental and predicted yield of maltenes during evaporation process
Appendix I

Mass transfer considerations

Mass transfer includes two processes, one involving the transfer of a product from its generation site to the external surface of the particle (intra-particle mass transfer) and the transfer of the molecule from the external particle-surface to the bulk of the gas. If mass transfer effects exist, they will be considered from the intra-particle mass transfer. A reason for this is that as the system presented in this work is under atmospheric pressure, then it is considered that when the products are on the surface of the particle the time required to transport the molecule to the bulk of the gas is larger than the time of reaction.

To establish if the intra-particle mass transfer it is important, this study made an approximation of the Thiele modulus ($\phi_1$) for first-order reactions and sphere particles. Thieles modulus is a measure of the ratio of the surface reaction rate to the rate of diffusion through the sand particles, when ($\phi_1$) is large, internal diffusion usually limits the overall rate of reaction; when ($\phi_1$) is small, the surface reaction is usually rate-limiting. The Thiele modulus for first order reactions and spheres particles is calculated as:

$$\phi_1 = \frac{R}{3} \times \sqrt{\frac{k_1}{D_e}} \tag{I.1}$$

Where $R$ is the radius of the particle, cm; $k_1$ is the rate of reaction, $s^{-1}$ and $D_e$ is the effective diffusivity $cm^2/s$. With $D_e$:

$$D_e = \frac{D_{AB} \times \varphi_p \times \sigma_c}{\tau} \tag{I.2}$$

Where $\varphi_p$ is the porosity; $\sigma_c$ is the constriction factor and $\tau$ is the tortuosity. The radius of the spheres is taken ranged between 125 $\mu$m to 250 $\mu$m (because of the size of the sand particles, 250 $\mu$m to 500 $\mu$m), the diffusivity for gases such as CH$_4$, H$_2$O, H$_2$, C$_2$H$_4$ and C$_2$H$_6$ in the mixture (oil/sand) of about $1 \times 10^{-8} \ cm^2/s$. Molecules in the volatiles (distillables and LMWM) range diffuse more slowly.
in the mixture phase because of their size molecules. Although the diffusion is not known they could be in the range of $1 \times 10^{-10} \text{cm}^2/\text{s}$. The reaction rate was taken as $1 \times 10^{-6} \text{s}^{-1}$ [8] and the porosity is supposed of 0.4.

With these, Thiele modulus ranged between 0.07 and 0.12 for gases and 0.71 and 1.18 for volatiles. According to these values the system is reaction-limited. The points established above are a first approximation; further work has to be carried out in order to establish if the effect of the mass transfer is still negligible at higher temperature when the mixture sand/oil becomes compact because of maturation of species to coke.