CONCEPTUAL DESIGN OF A PALM OIL HYDROTREATMENT REACTOR FOR COMMERCIAL DIESEL PRODUCTION

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Medellín, Colombia
2014
CONCEPTUAL DESIGN OF A PALM OIL HYDROTREATMENT REACTOR FOR COMMERCIAL DIESEL PRODUCTION

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

M.Sc. in Chemical Engineering

Supervisor:
Alejandro Molina

Research group:
Bioprocesos y Flujos Reactivos

Universidad Nacional de Colombia, Sede Medellín
Facultad de Minas
Medellín, Colombia
2014
A reactor with an industrial production of renewable diesel via palm oil hydrotreatment was conceptually designed based on laboratory-scale continuous and semi-batch reactor experiments. The conversion of vegetable oil to biodiesel through transesterification is responsible for a reduction in the use of a significant fraction of fossil fuels. Unfortunately, the diesel produced by transesterification has limitations such as high density, high viscosity and low cetane number. An alternative to transesterification is the hydrotreatment (HDT) of vegetable oils to produce a fuel with properties more similar to petroleum diesel than those of diesel obtained by transesterification. This thesis presents hydrotreating as an alternative for the production of renewable diesel in Colombia. It proposes a reaction pathway for hydrotreatment based on experiments with Refined, Bleached and Deodorized Palm Oil (RBDPO) and using a commercial solid trilobite NiMo catalyst (NiMo/γ-Al₂O₃, Haldor Topsøe TK-561 BRIM®). The experiments were carried out in a Parr reactor (V=250 mL) operating in semi-batch mode, at temperatures varying from 335°C to 365°C and hydrogen pressures in the range of 30 bar to 60 bar. Although in these experiments hydrogenation was evidenced by the production of C13-C19 alkanes conversion was low and it was possible to analyze intermediate species such as fatty acids and monoglycerides. The analysis of these intermediate species supported the proposal of a reaction pathway. Examples of the reaction steps in the pathway are: saturation of triglycerides, production of fatty acids, hydrodeoxygenation (production of C14, C16 and C18) and hydrodecarboxylation (production of C13, C15, C17 and C19). The physical-chemical characterization of the liquid and gaseous products was carried out with micro GC and gas chromatography coupled with mass spectrometry MS-GC, respectively. The results showed a preference to the reaction of hidrodecarboxylation, as demonstrated by the high proportion of odd to even hydrocarbons chains.

To take quantitative experimental data of the liquid-phase concentration suitable for the evaluation of kinetic parameters a laboratory-scale (stainless steel tube, 1/2-inch OD and 50 cm long), Trickle Bed Reactor (TBR), packed with 1.5 g fresh catalyst was used. The operating conditions and the metho-
dology for the characterization of the products of reaction were the same as those of the semi-batch experiments except for the additional use of MS-FID for liquid quantification. The experimental results showed high yield for hydrocarbons in the C15-C18 range corresponding to hydrodecarboxylation and hydrodeoxygenation. According to the characterization of the feedstock, reaction products and the reaction pathway proposed with the semi-batch data a kinetic mechanism that describes the palm oil hydrotreating process was proposed. The kinetics parameters for the six reactions were determined after a least-squares optimization of the difference between model and experimental results.

The kinetic parameters were used in two case studies that evaluated two different reactor configurations through simulations carried out in ASPEN V8.6. The physicochemical properties of palm oil and the reaction products were taken from the literature and a database available in ASPEN V8.6 respectively. Both reactor configurations guarantee adequate conversion of vegetable oil to hydrocarbons. However, while one demands a catalyst weight of 2232 kg for obtain a high conversion of RBDPO, the second achieves this through a lower catalyst weight, with a higher temperature of the thermal fluid but is necessary hydrogen quenching to avoid high temperatures that can cause products degradation; therefore, the second case is the recommended configuration.

Keywords: Vegetable oil, hydrotreating, trickle bed reactor, renewable diesel.
RESUMEN

Un reactor con una producción industrial de diesel renovable a través de hidrotratamiento de aceite de palma fue diseñado conceptualmente con base a experimentos en reactores contínuo y semi-batch a escala laboratorio. La conversión a biodiesel mediante el proceso de transesterificación es responsable de la sustitución de una fracción significativa de los combustibles fósiles a los biocombustibles. Desafortunadamente, el diesel producido por transesterificación tiene limitaciones, tales como la alta densidad, alta viscosidad y bajo número de cetano. Una alternativa a la transesterificación es el hidrotratamiento (HDT) de aceites vegetales para producir un combustible con propiedades más similares a las del diesel del petróleo y a las del diesel obtenido por transesterificación. Esta tesis presenta el hidrotratamiento como una alternativa para la producción de diesel renovable en Colombia. Inicialmente se propone una ruta de reacción de hidrotratamiento basado en experimentos con Aceite de Palma refinado, blanqueado y desodorizado (RBDPO) y usando un catalizador NiMo sólido comercial en forma de trilobita (NiMo/γ-Al₂O₃, Haldor Topsøe TK-561 BRIM®). Los experimentos se llevaron a cabo en un reactor Parr (V = 250 ml de apertura) operado en el modo semi-batch a temperaturas que varían desde 335°C a 365°C y presiones de hidrógeno en el intervalo de 30 bar a 60 bar. En estos experimentos la hidrogenación se llevó a cabo exitosamente ya que se produjeron alcanos C13-C19. También se produjeron especies intermedias tales como ácidos grasos y monoglicéridos. Las etapas de reacción en la ruta de reacción son: saturación de los triglicéridos, la producción de ácidos grasos, hidrodesoxigenación (producción de C18, C16 y C14) e hidrodecarboxilación (producción de C19, C17, C15 y C13). La caracterización físico-química de los productos líquidos y gaseosos se llevó a cabo mediante un micro GC y cromatografía de gases acoplada a espectrometría de masas MS-GC, respectivamente. Los resultados mostraron una preferencia a la reacción de decarboxilación, como lo demuestra la alta proporción de cadenas impares sobre las cadenas pares de hidrocarburos.

Para considerar datos experimentales cuantitativos de la concentración de compuestos en fase líquida adecuados para la optimización de los parámetros cinéticos, un reactor a escala laboratorio (tubo de ace-
ro inoxidable, 1/2 pulgada de diámetro externo y 50 cm de largo), tipo Trickle Bed (TBR), empacado con 1.5 g de catalizador fresco. Las condiciones de operación y la metodología para la caracterización de los productos de la reacción fue la misma que para los experimentos en semi-batch excepto por el uso adicional de MS-FID para la cuantificación de los componentes en la fase líquida. Los resultados experimentales mostraron un alto rendimiento de hidrocarburos C15-C18 correspondiente a las reacciones de hidrodecarboxilación e hidrodesoxigenación. De acuerdo con la caracterización de la materia prima, los productos de reacción y de la ruta de reacción propuesta con los datos en semi-batch se propuso un mecanismo cinético que describe el hidrotratamiento de aceite de palma. Los parámetros cinéticos para las seis reacciones se determinaron mediante la minimización del error cuadrático medio de la diferencia entre el modelo y los resultados experimentales.

Los parámetros cinéticos se utilizaron en dos casos de estudio que evaluaron dos diferentes configuraciones de reactor a través de simulaciones realizadas en ASPEN V8.6. Las propiedades fisicoquímicas del aceite de palma y los productos de reacción fueron tomados de la literatura y de la base de datos disponible en ASPEN V8.6 respectivamente. Ambas configuraciones de reactor garantizan la conversión adecuada de aceite vegetal a los hidrocarburos. Sin embargo, mientras que uno demanda un peso de catalizador de 2232 kg para obtener una alta conversión de RBDPO, el segundo logra este objetivo con una carga de catalizador menor, con una mayor temperatura del fluido térmico pero es necesaria una inyección de hidrógeno para evitar que las altas temperaturas degraden los productos, por lo tanto, es la configuración recomendada.

Palabras clave: Aceite Vegetal, hidrotratamiento, reactor tipo trickle bed, diesel renovable.
In memory of my grandfather Miguel Ángel Vélez

En memoria de mi abuelo Miguel Ángel Vélez
Acknowledgements

I would like to thank the following people, programs and institutions that contributed to the realization of this thesis.

I want to express a specially gratitude to my supervisor Professor Alejandro Molina. His excellence, constancy and dedication are an example to follow. Thanks for helping with the problems, we faced and not resting until the goal was achieved. His support and attitude towards his students always allowing them to shine and succeed is worthy of the utmost admiration. He never hesitated to invite me to the JICA business lunches and thank you very much for the time we shared.

Dr. Koji Sakashita, Professor Sachio Asaoka and Professor Atsushi Ishihara for sharing me their wide experience in chemical processes. They were always willing to help me with my research. They not only told me about their academic life but also Japanese culture and we exchanged gifts from both our cultures. They always treated me with great respect and good humor.

Professor Diana López, for allowing me to use the facilities and equipment of her group QUIREMA at Universidad de Antioquia, for batch and continuous experimental studies setup and characterization. Gina Hincapié, Angélica Forjionny, Juan David Tapia and Oswaldo Pérez, for their patience, dedication and their valuable contributions to this work specially in the experimental setup. They were always willing to help me, not only with my research but also offered me their friendship. I also thank the members of the QUIREMA group.

My colleagues and friends from the research group Bioprocesos y Flujos reactivos for their patience and time, primarily to Luis Carlos López, Juan Guilleromo Ramírez, Cesar Camilo Mendoza and Juan José Arias Belduque for their assistance and contributions.
To “Jóvenes Investigadores e Innovadores” COLCIENCIAS 2012 program by partially funding this project.

To “Beca de Exención de Derechos Académicos de Posgrado de la Facultad de Minas 2013” by partially funding this project.

To “Programa Nacional de Apoyo a Estudiantes de Posgrado para el Fortalecimiento de la Investigación, Creación e Innovación de la Universidad Nacional de Colombia 2014” program by partially funding this project.

To “JICA - Colombia” by partially funding this project.

To Haldor Topsøe and Saceites S.A.S. for to supply the catalyst and the RBDPO respectively.

Last but not least. I want to express my gratitude to all my friends who said: “Hey, Pipe, I found a great paper for your research the other day but I cannot find it now”. I thank the people that never wavered in their support or their respect for my work, for always being there in the most stressful moments, for all of this and for their love, friendship and admiration I am grateful every day of my life. My parents Ana and Juan, my uncles, Pedro, Hernán and Alberto, my aunts Nohelia, Virginia, Lina and Himelda, my brother Carlos, my girlfriend Estephanía and my friends: Lui Calo, Juan Gui, El Rolo, Adri, El Clark, Limonarias, Isa, Kevin, Julián, Mate, Ricardo, Chucho, Ginator, Angie, Tapias, Vivi, Macías, Christian, Javier and The Fish...They were always willing to help me move forward with their unwavering support, making me feel like an extremely lucky man.
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Physical constants

<table>
<thead>
<tr>
<th>Gravity</th>
<th>$g = 9.81 , m , s^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas constant</td>
<td>$R = 0.008314 , kJ , K^{-1} , mol^{-1}$</td>
</tr>
</tbody>
</table>
Symbols

- \( r'_i \): Reaction rate based in catalyst weight of species \( i \)  \( \text{kmol/kg} - \text{s} \)
- \( \rho_{\text{bulk}} \): Catalyst bulk density  \( \text{kg/m}^3 \)
- \( A \): Reactor cross section  \( \text{m}^3 \)
- \( v_o \): Total volumetric flow  \( \text{m}^3 \)
- \( E^j_a \): Energy activation of reaction \( j \)  \( \text{kJ/kmol} \)
- \( k^j_0 \): Pre-exponential factor of reaction \( j \)  \( 1/\text{s} \)
- \( F_i \): Molar flow of species \( i \)  \( \text{kmol/s} \)
- \( r_i \): Reaction rate of species \( i \) per unit of volume  \( \text{kmol/m}^3 - \text{s} \)
- \( C_i \): Concentration of species \( i \)  \( \text{kmol/m}^3 \)
- \( v_o \): Total volumetric flow  \( \text{m}^3 \)
- \( C_{P,A}^l \): Liquid heat capacity of fragment \( A \) in the triglyceride for temperature dependency  \( \text{J/kmol} - \text{K} \)
- \( N_{\text{frag}} \): Number of fragments in the triglyceride -
- \( x_A \): Mole fraction of fragment \( A \) in the triglyceride -
- \( V_A^l \): Liquid molar volume of fragment \( A \) in the triglyceride for temperature dependency  \( \text{m}^3/\text{kmol} \)
- \( \mu^l \): Liquid viscosity of fragment \( A \) in the triglyceride for temperature dependency  \( \text{Pa} - \text{s} \)
- \( G \): Superficial mass velocity, mass flux  \( \text{kg/m}^2 - \text{s} \)
- \( \rho \): Gas density  \( \text{kg/m}^3 \)
- \( d_p \): Diameter of particle  \( \text{m} \)
$\phi$  Porosity
Chapter 1

Introduction

1.1. Motivation

The increase of the energy demand has generated different options for the production of biofuels from renewable sources [1] due to the search for alternatives to minimize the dependence on fossil fuels. Vegetable oil is one of the most attractive alternatives for obtaining liquid fuels via different industrial ways [2,3]. One of them is the production of biodiesel by transesterification of palm oil due to its high production in Colombia [4], but the physical-chemical properties of the final product such as the high viscosity, high density, low cetane number and low energy content limit its use [5–7]. To be able to use this fuel a solution must be made mixing, 5-10%vol biodiesel in petroleum-derived diesel [8]. Unfortunately, this combination with petroleum diesel, only decreases, but does not eliminate, some of the main problems of using diesel such as sulfur oxides and nitrogen emissions and general fossil fuels dependence [6,7].

Recently the Hydrotreatment (HDT) process is used to convert vegetable oils to biofuel and light alkane gases. Renewable diesel production through hydrogenation of vegetable oils has advantages over transesterification processes, because the final product has a higher cetane number, better cold properties, higher calorific value and very important advantages as the final products are hydrocarbons while in transesterification are Fatty acid Methyl Esters (FAMEs). The first are similar to diesel from petroleum refining while the second are oxygenated compounds. Also the HDT of vegetable oil (HVO) subproduct, propane, has commercial advantages over glycerol (a subproduct in the transesterification) [1–3,5–7,9,10].

Typically HVO takes place at high pressures (> 20atm) and temperatures close to 350°C and involves hydrogen addition to break big-size triglycerides molecules of vegetable oil in the presence of a solid
catalyst [11–13]. As a result of this reaction, the big molecules in the oil decrease in size and become a mixture similar to petroleum diesel.

The HVO is a complex process because of the large number of phenomena and competitive reactions involved. This causes high operational complexity and costs. HDT involves the interaction of three phases: hydrogen, palm oil and catalyst besides requiring high temperatures and pressures. This process involves vegetable oil and hydrogen corresponding to two different phases that undergo changes and interact with themselves and with a catalyst that is a third solid phase. When these complex interactions occur, chemical engineering traditionally uses a trickle bed reactor (TBR). This complex reactive system normally takes place industrially in the same reactors designed for hydrodesulfurization, hydrodearomatization and hydrodenitrogenation reactions in the refinery processes [11,13,14].

Previous studies have proposed different models to describe the HVO process, some of them describe the HVO reactions with different pathways [2,15–20] and have, mostly, studied the performance of various catalyst that are currently being tested in this area [17,20–36] or co-processing vegetable oils with petroleum derivatives [37–39]. Others make use of global reactions neglecting mass transfer limitations to represent different phenomena [40]. However, there have been few studies [40–45] about the performance of the reactor itself. In Colombia, in particular, some authors [5] have modeled HDT of crude palm oil but, in the refereed literature, none have carried out not kinetic reaction studies when hydrotreating palm oil. The sketchy of detailed kinetic mechanisms allows only a general description, which is not desirable because of the potential importance of the temperature in the reactor as decomposition may occur when products reach a temperature over 370°C [16] or because partial conversion may yield products that affect the general reactor’s performance.

The aim of the present work is to present a first approximation to the design of a reactor for renewable diesel production at industrial scale. The conceptual design was made according to the typical balances of mass, energy and pressure drop equation and took special care to maintain a proper temperature in the reactor that prevented degradation while allowing for a high conversion.

This thesis does not follow the traditional format that has a general methodology section followed by results and discussion, but is divided in three parts. Each part has its own methodology and results section.
Chapter 3 proposes a reaction mechanism based on experiments conducted in a semi-batch reactor setup. Being the first chapter, it also describes in detail the feedstock as well as the catalyst used in the experiments and that are used through the text.

Chapter 4 presents results from a continuous TBR laboratory-scale reactor from which experiments were conducted to estimate kinetic parameters that could describe the hydrotreatment of palm oil.

The last chapter, number 5, describes the conceptual design of the hydrotreatment reactor. Two case studies were implemented to illustrate the design process. Simulations conducted in the software ASPEN PLUS V8.4 were used in the design.
1.2. Research objectives

1.2.1. Main Objective

To design a palm oil hydrotreatment trickle bed reactor for commercial diesel production.

1.2.2. Specific objectives

- To formulate kinetic mechanisms for palm oil hydrotreatment in the process of commercial diesel production.
- To develop a simulation that represents the palm oil hydrotreatment.
- To determine the feedstock properties, the reactor dimensions and operating conditions that allow the commercial diesel production from vegetable oil.
Chapter 2

Fundamentals and Background

The renewable diesel production from vegetable oils is carried out in typical hydrotreating units [1–3], at conditions similar to those used in hydrogenation of fractions of crude oil. The hydrotreatment of fractions of crude oils is one of the most important processes in petroleum refining because it removes contaminants such as sulfur, aromatics and nitrogen from fossil fuels. The most typical reactor configuration in the HDT process is a TBR [11–14].

This chapter describes important technical aspects related to TBRs and, particularly, to their application for renewable diesel production. This chapter presents as well general considerations regarding reaction mechanisms and previous kinetic studies for the HVO process.

2.1. Trickle Bed Reactor

Trickle Bed Reactor is a type of packed bed reactor, in which multiple phases coexist, flow and undergo a chemical reaction in a catalytic vertical column bed. The reaction occurs between the gas and the adsorbed liquid on the catalyst surface. TBR presents two different types of configuration: co-current downflow as shown in Figure 2.1 a), or the gas is introduced in a countercurrent upflow as shown in Figure 2.1 b) adapted from reference [11]. The more-applied design is co-current downflow. Cocurrent downflow trickle bed reactor is closer to plug flow, because the interaction between the solid and liquid phase is similar to shedding [11–13].
The gaseous phase flows continuously while the liquid phase has downflow through the catalyst bed like a film, spray or bubbles. The regime depends on the flow rate of the phases as shown in Figure 2.2, adapted from reference [46].
**Figure 2.2:** Schematic illustration of the location of the trickle, mist, bubble and pulsing flow regimes with respect to gas and liquid flow rates.

Table 2.1 adapted from reference [11] shows some advantages and disadvantages of the different configurations of trickle bed reactor:
Table 2.1: Trickle bed reactor advantages and disadvantages for the different configurations of gas flow.

<table>
<thead>
<tr>
<th>Trickle bed cocurrent reactor</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- The liquid flow is close to plug flow</td>
<td>- Liquid maldistribution, channeling and incomplete catalyst wetting</td>
<td></td>
</tr>
<tr>
<td>- Operation at high pressures and temperatures</td>
<td>- Limitations on the use of viscous liquids due to the risk of increasing the pressure drop through the bed</td>
<td></td>
</tr>
<tr>
<td>- Wide range of flow regimes</td>
<td>- In exothermic reactions, hotspots can form</td>
<td></td>
</tr>
<tr>
<td>- Low pressure drop</td>
<td>- Difficulties in extracting heat for relatively fast reactions</td>
<td></td>
</tr>
<tr>
<td>- Compared with the countercurrent flow, the flooding phenomenon does not occur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- The gas feedstock can be higher than countercurrent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Facilitates the gas interaction in the reaction system</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trickle bed countercurrent reactor</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- It is preferred for high heats of reaction</td>
<td>- At high flow liquid can cause flooding</td>
<td></td>
</tr>
<tr>
<td>- It develops a better axial thermal profile</td>
<td>- The estimation of the pressure drop, mass transfer coefficients, and the retained liquid (liquid holdup) cannot be describes with more mathematically simplicity than cocurrent TBRs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Effects of axial and radial dispersion in the liquid phase</td>
<td></td>
</tr>
</tbody>
</table>
Trickle bed reactors are commonly used in petrochemical processes such as those reported in Table 2.2, adapted from references [11–13]. The addition of gases at high pressures and temperatures saturates and breaks weak bonds, cracks and isomerizes molecules to form the desired products. In the case of hydrogenation of compounds having double or triple bonds, carbonyl, nitrogen and sulfur are saturated by addition-substitution or elimination reactions to produce lighter compounds [11,12,12,13].

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Process</th>
<th>Catalyst</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation</td>
<td>Ethanol oxidation</td>
<td>Pd/Al</td>
<td>20</td>
<td>70-100</td>
</tr>
<tr>
<td></td>
<td>Wet oxidation of phenol</td>
<td>Pt/Al₂O₃</td>
<td>30-100</td>
<td>100-200</td>
</tr>
<tr>
<td>Hydrodesulfurization</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrodenitrification</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petroleum processing</td>
<td>Hydrodemetallization</td>
<td>Co-Ni</td>
<td>10-20</td>
<td>320-380</td>
</tr>
<tr>
<td></td>
<td>Catalytic hydrocracking</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Catalytic dearomatization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>Hydrogenation of petroleum fractions,</td>
<td>Pd, Pt, Ni</td>
<td>30-100</td>
<td>30-100</td>
</tr>
<tr>
<td>reactions</td>
<td>nitrocompounds,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>carbonyl compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactions</td>
<td>Hydrogenation of 2-butyne-1,4-diol</td>
<td>Ni</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>Hydrogenation of aniline to cyclohexylaniline</td>
<td>Pd/Al₂O₃</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Hydrogenation of glucose to sorbitol</td>
<td>Ru/C</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Hydrogenation of maleic anhydride</td>
<td>Pt/C</td>
<td>10-50</td>
<td>80</td>
</tr>
<tr>
<td>F-T synthesis</td>
<td>Fischer-Tropsch reaction</td>
<td>Co/TiO₂</td>
<td>20</td>
<td>170-370</td>
</tr>
</tbody>
</table>

The liquid phase continuously flow downwards through the catalytic bed as film, mist or bubbles. The flow pattern depend on the flow properties most significantly on the velocity of each phase. The hydrodynamics of the liquid and gas phases flowing through a packed column are very complex and can cause operational problems, such as those described in Table 2.3 [11–13].
From the viewpoint of reaction engineering, the design of packed columns with two phase flow should minimize mass transfer limitations to ensure correct development of the reaction kinetics in the system. Thereby, for easier modeling and reactor design, it is custom to design reactors with a long axial axis for the catalyst beds (industrially 10 - 30 m) and low liquid velocity, to promote plug flow for both phases in the reactor [11–13].

2.1.1. Thermal Effects

Thermal gradients in the reactor, if the diameter of the reactor is too large and the reaction is exothermic can cause “hots-pots”. The hot-spot must not exceed the operating range of the catalyst or the temperature of product degradation. These hot-spots can be eliminated with quenching of the gas phase, as shown in Figure 2.3 in the case of hydrogenation of hydrocarbons [11,12].
Biodiesel production is seriously affected by temperature. As showed Huber et al. [16], the maximum production of diesel-like alkanes occurs between 330°C and 370 °C. However, at this higher temperature the process starts to yield isomerized and cracked products.

2.1.2. Plug Flow Deviations

Traditionally TBRs are designed under perfect plug flow criteria, which allows a more mathematically simple representation of the behavior of the reactor as the mass and radial thermal dispersion are neglected in the modeling. Normally high temperature gradients are the reasons for deviations from ideal plug flow, which in the case of a PFR (Plug Flow Reactor) may cause channeling or bypass. These phenomena interfere with the reaction process. In TBRs the liquid radial dispersion is not significant due to the low liquid velocity, so it is possible to assume plug flow if the bed is well-packed (constant porosity).
2.2 Pathway and kinetics mechanisms of hydrotreatment of vegetable oils: An overview

Regions close to the wall are generally less packed, so the flow may be more abundant at the wall and cause radial and axial dispersion. This analysis suggests that a trickle bed reactor may be considered a PBR (Packed Bed Reactor) although it is hydrodynamically more complex.

One of the most important components of a conceptual design of any reactor is the reaction mechanisms and kinetics. The next section describes the current state of the art of the understanding of the chemical reactions taking place in the HVO as well as the kinetic expressions.

2.2. Pathway and kinetics mechanisms of hydrotreatment of vegetable oils: An overview

Vegetable oils are composed mainly by triglycerides. Esters composed of three esterified fatty acids. Figure 2.4 shows an example of a triglyceride. The red frame enclosures the esterified fatty acids. The carbon chain of the acid is named based on the number of carbon atoms from the α carbon to the final carbon as R (#C), where #C represents the number of carbon atoms. For this case, the triglyceride molecule is composed of R16, R18 and R18:1 respectively. The three fatty acids can be different or all the same. This research assumed that triglycerides in the sample palm oil are composed of the same fatty acids.

It has been reported [2, 15–20] that intermediate products during the HVO are mainly diglycerides, monoglycerides and fatty acids. Figure 2.5 presents an example of the saturated acid glycerides. It should be noted that the depiction of mono - and diglycerides is particular of the HDT process and is a mistaken idea, because a correct mono or diglycerides the oxygen of ester bond remains as OH group in the molecule. Transesterification process have a correct nomenclature for the molecules of mono - and diglycerides.
Many studies [2, 15–20, 41–43, 45, 47] have proposed different pathways to describe the HVO process. The most studied vegetable oils are rapeseed [25], cottonseed [40], pomace oil [48], sunflower [10], palm [5, 39, 49–51], jatropha [20, 51] and coconut [52]. Most studies [2, 15–20] agree that the triglycerides in vegetable oil are first saturated, e.g. the chain R18:1 in Figure 2.4 in the triglyceride are hydrogenated to R18:0. Then a saturated triglyceride is hydrogenated and subsequently produces a diglyceride and a fatty acid. The hydrogenation of diglycerides produces a monoglycerides and a fatty acid too. Finally the
2.2 Pathway and kinetics mechanisms of hydrotreatment of vegetable oils:
An overview

hydrogenation of a monoglyceride produces a fatty acid and a propane molecule. Simultaneously with the diglycerides and monoglycerides hydrogenation the fatty acids react via hydrodeoxygenation and decarboxylation to produce even and odd alkanes, respectively, as shown in Figure 2.6 [2,15–20]. Other important area of study in HVO is devoted to evaluate the performance of various catalyst such as zeolites [2,18,19,29,30], NiMo [17,20,22,26–31,33–36], CoMo [17,20,26–29,33,35,36], Pd [25,28,29,31,35,36] and Pt [20,24,27,28,35].

![Figure 2.6: General pathway for the hydrogenation of triglycerides](image)

Several authors present the kinetic parameters for hydrotreating reactions of vegetable oils. Some exceptions are Sebos et al. [40], Vonortas et al. [39], Anand et al. [41], Kubička [42], and Snäre et al. [45]. Sebos describes the HVO reaction as an overall reaction but does not present a reaction pathway itself. Sebos developed a first-order kinetic model to estimate the conversion of esters (triglyceride) of cottonseed oil with CoMo/γ-Al₂O₃ catalyst. The model was validated at temperatures between 305°C to 345°C, with pressures close to 30 bar at weight hourly space velocities (WHSV) of 5 h⁻¹ to 25 h⁻¹. For WHSV under 5 h⁻¹ the conversions was close to 100%. The activation energy for hydrodeoxygenation was 111 kJ/mol. Vonortas co-hydrotreated mixtures of gasoil - 30% palm oil/AVO over NiMo/γ-Al₂O₃ catalyst. The ex-
periments were carried out in a bench-scale trickle-bed reactor at $T = 310 - 350^\circ\text{C}$ with a total pressure $P = 33$ bar. The focus of the kinetic study was the hydrodesulphurization (HDS) reaction as limitant step of the co-hydrotreating reaction. Anand describes a kinetic study of hydrocracking of jatropha oil over sulfided CoMo/$\gamma$-$\text{Al}_2\text{O}_3$ catalyst. The mechanism include reactions of HDO and oligomerization but does not include specific components. The mechanism is developed by groups of components for the reactive as triglycerides and for the products such as alkanes, theses are divided by light (C5-C8), middle (C9-14), heavy (15-18) and oligomerized (> C18). Kubička has a very complete kinetic study of rapeseed oil transformations of HDO, with experimental work in a laboratory trickle-bed reactor. The kinetics mechanism of triglycerides hydrogenation include some intermediates that were not found in this research such as some alcohols ($C_{17}H_{35}CH_2OH$), also include reactions such as the production of diglycerides from alcohol and acids. Snåre describes the HVO of triglycerides by reaction of ethyl sterate decarboxylation in a semi-batch reactor over Pd/C catalyst and describes a complete kinetic study of this reaction with some intermediates such as stearic acid and as final products heptadecane C17 (aliphatic), olefins C17 and aromatic C17. Another important research in Colombia in particular was that by Guzman et al [5], who modeled HDT of crude palm oil and proposed a detailed pathway with specific compounds but, without specific kinetic data. They describe palm oil reactions by equilibrium calculations. The aforementioned literature review suggest that there are not studies that have presented a complete description of a kinetic mechanism for the HDT of palm oil. The sketchy of detailed kinetic mechanisms only allows a general description for a industrial reactor design.

### 2.3. Summary

The reactor typically used to carry out the HVO are the TBRs, this kind of reactors are characterized mainly by the low velocity for the liquid flow, therefore reducing any deviations from plug flow such as channeling. The most used configuration for TBR is co-current down-flow. If exothermic reactions are present in the TBR, a hot-spot may occur. To prevent such event most HVO TBRs take advantage of gas quenching.

The reaction pathway that represents the vegetable oil hydrogenation follows mainly two routes: hydrodeoxygenation and decarboxylation. The triglycerides present in the palm oil are nearly always esterified fatty acid (i.e. palmitic or stearic) of even-carbon-number chains. Therefore, hydrodeoxygenation yields
even-carbon-number hydrocarbons but decarboxylation only yields odd-carbon-number hydrocarbons. The only exception to this rule is when high temperatures cause cracking. In this case there is not a specific rule for the number of carbons in the products [16].

The refereed literature does not present detailed kinetic mechanisms for the hydrogenation of palm oil hydrogenation. Most studies solely present general steps such as: conversion of monoglycerides to hydrocarbons [45], an overall reaction for triglycerides hydrogenation [40], equilibrium calculations [5], and production of hydrocarbons from triglycerides [41] some of them include alcohols formation [42]. While adjusting these scarce kinetic data for the HDT of Colombian palm oil is a possibility, it seems very desirable to conduct a kinetic evaluation of the system before an industrial reactor design.
Chapter 3

Reaction pathway for the hydrogenation of palm oil

This chapter describes a reaction pathway for the hydrogenation of palm oil based on experiments carried out in a semi-batch reactor. A reaction pathway is considered as a first step towards the conceptual design of the reactor as it is the keystone for the proposal of kinetic expressions.

The beginning of this chapter describes the palm oil used through the thesis and compares relevant physicochemical properties to those of other HDT feedstock reported in the literature. Section 3.2 presents the experimental setup of the semi-batch reactor and a final section presents the composition of the liquid products and the reaction pathway.

3.1. Feedstock: Refined Bleached Deodorized Palm Oil, RBDPO

Colombia is one of the largest palm oil producers in South-America and the world; therefore, vegetable oil hydrotreating seems very attractive. Most palm oil producers sell an unrefined liquid that has limited uses in the food and cosmetic industry. The use of this unrefined oil in hydrotreating will pose multiple problems [49] because of inhibitors build up and secondary reactions. However, a refined version of this oil (refined bleached deodorized palm oil, RBDPO) is also available in the market and can readily be used in hydrotreatment.
RBDPO contains refined fatty acids compounds in palm oil, without volatile species such as aldehydes and ketones, colored species such as oxides, phospholipids and metals are removed as well [49]. A RBDPO sample was supplied by a local company Saceites S.A.S. [53] and characterized by the PFA Laboratory [54] at Universidad de Antioquia using MS-FID. The composition was determined by transesterification of the oil with methanol followed by quantification of the resulting fatty acid methyl esters (FAMEs). The RBDPO composition in Table 3.1 is similar to that reported in literature [5, 39, 49–51] and contains four main triglycerides of the same carboxylic acid chain (tripalmitin, tristerain, triolein, and trilinolein). In all studies the oleic and palmitic fatty acids account for more than 80% of the RDBPO. The other significant components of RDBPO are linoleic and stearic fatty acids that corresponds to around 20%. The differences between the values for some fatty acids chains composition are probably due to the differences in the climatic conditions of the palm oil plantations of the different studies.

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Oleic</td>
<td>18:1</td>
<td>45.8</td>
<td>39.1</td>
<td>45.2</td>
<td>39.7</td>
<td>45.0</td>
<td>43</td>
<td>38.9</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16:0</td>
<td>37.4</td>
<td>44.3</td>
<td>40.8</td>
<td>44.5</td>
<td>43.0</td>
<td>42</td>
<td>34.6</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18:2</td>
<td>11.1</td>
<td>10.1</td>
<td>7.9</td>
<td>9.3</td>
<td>12.0</td>
<td>10.1</td>
<td>13.1</td>
</tr>
<tr>
<td>Stearic</td>
<td>18:0</td>
<td>3.6</td>
<td>5.0</td>
<td>3.6</td>
<td>3.8</td>
<td>4.0</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>Myristic</td>
<td>14:0</td>
<td>0.8</td>
<td>0.8</td>
<td>2.5</td>
<td>1.2</td>
<td>1.3</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Arachidic</td>
<td>20:0</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Lauric</td>
<td>12:0</td>
<td>0.4</td>
<td>0.3</td>
<td>0.8</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Linolenic</td>
<td>18:3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Eicosenoic</td>
<td>20:1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>16:1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Margaric</td>
<td>17:0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Lignoceric</td>
<td>24:0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Behenic</td>
<td>22:0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Pentadecanoic</td>
<td>15:0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
<td>99.9</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
3.2. Experimental setup: semi-batch reactor

The reactions were carried out in a semi-batch Parr autoclave reactor (V=250 mL), similar to that in references [48, 55], Figure 3.1 shows the experimental setup to perform the semi-batch HDT of palm oil. The system includes RBDPO, U.A.P Grade 5 (99.999% purity) hydrogen and commercial solid 1.8 mm trilobite NiMo catalyst (NiMo/γ-Al₂O₃, Haldor Topsøe TK-561 BRIM®) [56]. The catalyst presulfurization for activation and stabilization was carried out ex-situ with dimethyl disulfide (DMDS) at 400°C in a continuous reactor. The catalyst was exposed during nine hours to H₂S gases, product of the DMDS decomposition.

For every operating conditions in Table 3.2, 5 g of sulfided catalyst reacted with 95 g of RBDPO at the operating conditions in . The mixture catalyst/oil formed a slurry. Although a study of the distribution of the catalyst in the oil was not undertaken, the relatively strong agitation (350 rpm), not too high oil viscosity (0.57 cP at 350°C) and average density (899 kg/m³ at 350°C) suggest that for an impeller diameter of 0.5 cm and a reactor diameter of 6.3 cm the distribution of catalyst in the oil was acceptable. After loading the RBDPO and the catalyst, the reactor was sealed and heated with a temperature ramp of 2°C/min up to the operating temperature (between 335°C-350°C). Once the system was at the operating temperature, the reaction time was set to 0 min and the operating pressure was maintained constant at the values specified in Table 3.2, by a semi-continuous hydrogen flow. The reactive mixture was sampled at 10 min, 20 min and 30 min. The liquid products were mainly fatty acids and hydrocarbons that were analyzed with a GC-MS, previously calibrated using the response factor of an internal standard of octane dissolved in hexane. The gas products were characterized on-line with a micro-GC calibrated with a mixture with a known concentration of the gases. The conditions selected for the experiments were taken from previous studies in this area [5, 16, 49]. Temperature range was selected according with study of Huber et al. [16] for vegetable oil hydrotreatment, the pressure and the reaction time were selected according with typical operating conditions for RBDPO hydrogenation.
3.2 Experimental setup: semi-batch reactor

**Figure 3.1:** Experimental semi-batch setup for hydrotreatment of RBDPO
Table 3.2: Operating conditions in semi-batch reactor

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T[^\circ C]$</th>
<th>$P[\text{bar}]$</th>
<th>$t[\text{min}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>335</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>350</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>365</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>

3.3. Results and discussion

The reaction of RBDPO hydrogenation was successfully carried out. Not only C13-C19 alkanes were produced, but also intermediates such as palmitic, oleic and stearic acid and monoglycerides. The conversion of triglycerides was close to 60%. The production of alkanes was, however, too low. Figure 3.2 shows a typical chromatogram of the liquid sample. Appendix A shows all the chromatograms and mass spectra of samples and identified components, respectively. While the low yield of hydrocarbons is certainly a drawback for the use of this experimental setup to obtain kinetic parameters, it allows to elucidate a reaction pathway that describes the process.

Assuming that triglycerides follow a reaction pathway similar to that given in section 2.2, the proposed reactions steps were saturation of triglycerides, production of fatty acids, hydrodeoxygenation (C14, C16 and C18 production) and hydrodecarboxylation (C13, C15, C17 and C19 production).
Table 3.3 shows the identified liquid products of the hydrotreatment reactions. C13-14 hydrocarbons originate from myristic fatty acid chains, C15-16 from palmitic fatty acid chains, C17-18 from oleic fatty acid chains and C19 comes from arachidic fatty acid chains. The odd-carbon-number hydrocarbons result from triglycerides hydrodecarboxylation and the even-carbon-number hydrocarbons from hydrodeoxygenation reactions based on the pathway of Figure 2.6. The results show a preference to hydrodecarboxylation reactions, as evident by the high proportion of odd hydrocarbon chains (12% w/w) compared to the number of hydrocarbons with even chains (2.5% w/w). Although the liquid analysis system could not resolve diglycerides or triglycerides because these heavy species cannot be identified by the GC-MS, these species are retained by the injector of the equipment. The fact that only 54.2% of the initial mass of triglycerides
was accounted for in the spectrograms, suggests the presence diglycerides as intermediates in the reaction.

### Table 3.3: Identified components in liquid samples

<table>
<thead>
<tr>
<th>Identified components</th>
<th>Average composition [%w/w]</th>
<th>Fatty acid</th>
<th>Fatty acid chain</th>
<th>Retention time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C13 0.1 Myristic C14:0</td>
<td>9.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14 0.1 Myristic C16:0</td>
<td>12.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C15 5.3 Palmitic C16:0</td>
<td>14.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C16 1.1 Palmitic C16:0</td>
<td>17.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C17 6.4 Stearic C18:0</td>
<td>19.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18 1.3 Stearic C18:0</td>
<td>21.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C19 0.2 Arachidic C20:0</td>
<td>23.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmitic acid 22.9 Palmitic C16:0</td>
<td>25.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic acid 2.7 Oleic C18:1</td>
<td>28.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid 12.2 Stearic C18:0</td>
<td>29.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl palmitate (Monoglyceride R-16)</td>
<td>0.8 Palmitic C16:0</td>
<td>46.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl stearate (Monoglyceride R-18)</td>
<td>1.1 Stearic C18:0</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>54.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odd hydrocarbon chain</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Even hydrocarbon chain</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fatty acids</td>
<td>37.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Considering the RBDPO composition (Table 3.1), the identified compounds of the HVO reaction (Table 3.3), and the current understanding of hydrotreatment that was described in Section 2.2 a reaction pathway was proposed. The reaction process starts with the saturation of triglycerides, the hydrogenolysis of saturated triglycerides to fatty acids follows and, finally, hydrodeoxygenation and hydrodecarboxylation reactions are responsible for the production of alkanes. It is worth noting that the triglycerides degradation is not properly known as a mechanism, it represents an overall reactions to explain the fatty acids and alkanes production. Table 3.4 shows step by step the proposed pathway.
3.4 Summary

The hydrogenation of RDBPO was carried out in a semi-batch reactor. The low conversion to alkanes caused probably by poor mass transfer between the gas and the liquid phases was ideal to propose a reaction pathway for the process as intermediate species such as fatty acids and monoglycerides were identified.

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction Type</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td></td>
<td>( C_{57}H_{92}O_6 + 9H_2 \rightarrow C_{57}H_{110}O_6 )</td>
</tr>
<tr>
<td>R2</td>
<td>Hydrogenation of</td>
<td>( C_{57}H_{98}O_6 + 6H_2 \rightarrow C_{57}H_{110}O_6 )</td>
</tr>
<tr>
<td>R3</td>
<td>unsaturated</td>
<td>( C_{57}H_{104}O_6 + 3H_2 \rightarrow C_{57}H_{110}O_6 )</td>
</tr>
<tr>
<td>R4</td>
<td>triglycerides</td>
<td>( C_{51}H_{92}O_6 + 3H_2 \rightarrow C_{51}H_{98}O_6 )</td>
</tr>
<tr>
<td>R5</td>
<td></td>
<td>( C_{63}H_{116}O_6 + 3H_2 \rightarrow C_{63}H_{122}O_6 )</td>
</tr>
<tr>
<td>R6</td>
<td></td>
<td>( C_{51}H_{98}O_6 + 3H_2 \rightarrow 3C_{15}H_{31}COOH + C_3H_8 )</td>
</tr>
<tr>
<td>R7</td>
<td>Hydrogenolysis</td>
<td>( C_{57}H_{104}O_6 + 3H_2 \rightarrow 3C_{17}H_{33}COOH + C_3H_8 )</td>
</tr>
<tr>
<td>R8</td>
<td></td>
<td>( C_{57}H_{110}O_6 + 3H_2 \rightarrow 3C_{17}H_{35}COOH + C_3H_8 )</td>
</tr>
<tr>
<td>R9</td>
<td></td>
<td>( C_{51}H_{98}O_6 + 2H_2 \rightarrow C_{19}H_{38}O_2 + 2C_{15}H_{31}COOH )</td>
</tr>
<tr>
<td>R10</td>
<td></td>
<td>( C_{57}H_{110}O_6 + 2H_2 \rightarrow C_{21}H_{12}O_2 + 2C_{17}H_{35}COOH )</td>
</tr>
<tr>
<td>R11</td>
<td>Hydrodeoxygennation</td>
<td>( C_{45}H_{86}O_6 + 12H_2 \rightarrow 3C_{14}H_{30} + C_3H_8 + 6H_2O )</td>
</tr>
<tr>
<td>R12</td>
<td></td>
<td>( C_{51}H_{98}O_6 + 12H_2 \rightarrow 3C_{16}H_{34} + C_3H_8 + 6H_2O )</td>
</tr>
<tr>
<td>R13</td>
<td></td>
<td>( C_{57}H_{110}O_6 + 12H_2 \rightarrow 3C_{18}H_{38} + C_3H_8 + 6H_2O )</td>
</tr>
<tr>
<td>R14</td>
<td>Hydrodecarboxylation</td>
<td>( C_{45}H_{86}O_6 + 3H_2 \rightarrow 3C_{13}H_{28} + C_3H_8 + 3CO_2 )</td>
</tr>
<tr>
<td>R15</td>
<td></td>
<td>( C_{51}H_{98}O_6 + 3H_2 \rightarrow 3C_{15}H_{32} + C_3H_8 + 3CO_2 )</td>
</tr>
<tr>
<td>R16</td>
<td></td>
<td>( C_{57}H_{110}O_6 + 3H_2 \rightarrow 3C_{17}H_{36} + C_3H_8 + 3CO_2 )</td>
</tr>
<tr>
<td>R17</td>
<td></td>
<td>( C_{63}H_{122}O_6 + 3H_2 \rightarrow 3C_{19}H_{40} + C_3H_8 + 3CO_2 )</td>
</tr>
</tbody>
</table>
The main products present in the reaction were intermediate species such as fatty acids, monoglycerides and, probably, diglycerides. Table 3.4 presents the most probable reactions taking place in the system. After the saturation of triglycerides, they are converted to diglycerides, monoglycerides, fatty acids and alkenes through reactions of hydrogenolysis, hydrodecarboxylation and hydrodeoxygenation. A correct reaction pathway proposal for palm oil hydrogenation allows a good understanding of the process. This is a first step to propose kinetic expressions for the HVO in a TBR, a requirement in the design of an industrial-scale TBR.
Chapter 4

Estimation of kinetic parameters for the hydrotreatment reaction

This chapter presents first the experimental setup of a high-pressure TBR used to obtain the kinetic expressions for the hydrotreatment of palm oil. The analysis of the experimental results (composition of the liquid products) suggests new reactions for the reaction pathway and allows the proposal of a simplified mechanism from which kinetic parameters are calculated.

The experimental results in this chapter complement those obtained in Chapter 3 as probably mass transfer limitations in the semi-batch reactor caused by a combination of phenomena such as limited hydrogen diffusion as well as difficulties related to sampling probably caused the poor conversion of triglycerides observed in the previous section. The higher conversion achieved in the continuous TBR allows for the estimation of kinetic expressions.

4.1. Experimental setup: Trickle Bed Reactor for continuous hydrogenation of palm oil

For the development of a HVO kinetic model for an industrial reactor for renewable diesel production, it is preferable to collect the experimental data in a continuous reactor that guarantees higher conversion and behaves more similarly to an industrial reactor. Figure 4.1 shows the experimental setup for the continuous reactor. This system was completely designed in this research and is similar to that in references [29,30,57]. The reactive system includes the reactor (stainless steel vertical tube), a furnace, a
back pressure regulator to maintain constant pressure, and a mass flow controller. The RBDPO was fed to the reactor by a HPLC pump. It is worth highlighting that the RBDPO is semi-solid at Medellin room temperature, therefore it was necessary to develop a preheating procedure. First, the RBDPO storage vessel was covered with a heat tape at 65°C, also the pump suction and discharge tubing were covered with a heat tape at 85°C to prevent RBDPO solidification. The system also includes safety devices such as a check valve and a rupture disk. The same commercial solid trilobite NiMo catalyst used in semi-batch experiments was used. The operating procedure for the high pressure TBR is given in Appendix B. The temperature profiles through the reactor without chemical reaction in Appendix C show the region of the reactor that guarantees isothermal operation.

Figure 4.1: Experimental setup for continuous procedure
4.1 Experimental setup: Trickle Bed Reactor for continuous hydrogenation of palm oil

For all experiments the reactor was packed with 1.5 g of fresh catalyst supported by quartz wool and a quartz tube of 24 cm as Figure 4.2 illustrates. To control the exothermicity of the reaction, the catalyst was mixed with 1 g of quartz spheres with diameter 1 mm to obtain a total active bed height of 5 cm. 1 g of quartz spheres at the top of the reactor distributed the oil through the cross sectional area of the reactor. Catalyst presulfurization for activation and stabilization was carried out in situ at 400°C through DMDS bubbled with 100 SCCM (Standard Cubic Centimeters per Minute) of hydrogen during 13 hours. After catalyst sulfurization the reaction was carried out at the conditions showed in Table 4.1, these conditions were selected based on previous experiments described in references [5,16,49] and on the results obtained in the semi-batch reactor (Chapter 3). The RBDPO volumetric flow was calculated based on the catalyst weight and the desired liquid residence time. The hydrogen flow was estimated using a H₂/RBDPO molar ratio equal to 20 as recommended by previous studies on HVO conducted in the research group [58]. All reactions were conducted in duplicate, except for R7 that was carried out three times. The liquid and gaseous samples were characterized as previously described in Chapter 3.

![Figure 4.2: Experimental packed TBR](image-url)
4.2. Results and discussion

This section presents the results on RBDPO hydrogenation using a laboratory scale TBR. The first part presents the characterization of the liquid samples of the reaction products; the final part proposes adjustments to the reaction mechanisms described in the previous chapter and a simplified kinetics mechanism is proposed to represent the HVO process.

4.2.1. Hydrotreatment of palm oil in a continuous reactor

The main products of the RBDPO hydrogenation are alkanes in the range of C15-C18. Figure 4.3a) shows a typical chromatogram as results of the liquid sample for reaction 7 in Table 4.1. Appendix D presents the chromatograms of all the liquid products of the hydrogenation of RBDPO for the continuous set up. The concentration of C15 to C18 hydrocarbons is notably higher than that from the rest of species. Other species of lower concentrations are other hydrocarbons (C9 to C14 and C19 and C20) and palmitic acid. Not very evident in the chromatographs, Figure 4.3 b) also shows the presence of C21 to C24 hydrocarbons as well as oleic and stearic acids. Table 4.2 presents the characterization of liquid products using GC-MS for continuous RBDPO hydrotreatment at the operating conditions shown in Table 4.1. The identified compounds, the origin and the average retention time for the chromatogram are presented. The micro-GC results of gases analysis are not presented due to the hydrogen was in a high concentration and did not allow a correct lecture of the others gases($CO_2$ and propane) in the equipment.

### Table 4.1: Operating Conditions in the continuous reactor

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T[^{°}C]$</th>
<th>$P[bar]$</th>
<th>$\tau[min]$</th>
<th>RBDPO volumetric flow [$mL/min$]</th>
<th>$H_2$ Volumetric flow [SCCM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>335</td>
<td>60</td>
<td>30</td>
<td>0.07</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>60</td>
<td>15</td>
<td>0.14</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>60</td>
<td>30</td>
<td>0.07</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>350</td>
<td>60</td>
<td>45</td>
<td>0.05</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>30</td>
<td>30</td>
<td>0.07</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>350</td>
<td>45</td>
<td>30</td>
<td>0.07</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>365</td>
<td>60</td>
<td>30</td>
<td>0.07</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 4.3: Chromatogram of liquid sample of reaction 7 (see Table 4.1) in the laboratory scale TBR. a) Amplified Chromatogram
Table 4.2: Identified components in liquid products using a laboratory scale TBR

<table>
<thead>
<tr>
<th>Identified components</th>
<th>Origin</th>
<th>Fatty acid</th>
<th>Retention time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C9 Capric</td>
<td>C10:0</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>C10 Capric</td>
<td>C10:0</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>C11 Lauric</td>
<td>C12:0</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>C12 Lauric</td>
<td>C12:0</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>C13 Myristic</td>
<td>C14:0</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>C14 Myristic</td>
<td>C14:0</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>C15 Palmitic</td>
<td>C16:0</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>C16 Palmitic</td>
<td>C18:0</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>C17 Stearic</td>
<td>C18:0</td>
<td>16.4</td>
<td></td>
</tr>
<tr>
<td>C18 Stearic</td>
<td>C18:0</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>C19 Arachidic</td>
<td>C20:0</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td>C20 Arachidic</td>
<td>C20:0</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>Palmitic</td>
<td>C18:0</td>
<td>19.2</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>Oleic</td>
<td>C18:1</td>
<td>20.4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Stearic</td>
<td>C18:0</td>
<td>20.6</td>
</tr>
<tr>
<td>C21 Behenic</td>
<td>C20:0</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>C22 Behenic</td>
<td>C20:0</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>C23 Lignoceric</td>
<td>C20:0</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>C24 Lignoceric</td>
<td>C20:0</td>
<td>23.1</td>
<td></td>
</tr>
</tbody>
</table>

The species identified in the liquid products with GC-MS were quantified using GC-FID. Table 4.3 shows that for R3, R4 and R7 over 95% of total identified compounds are in the range of C15-C18 hydrocarbons. This shows how successful the hydrogenation reaction was. The 100% of the samples cannot be identified due to the same reason that in batch operation, i.e. the diglycerides and monoglycerides were retained in the injector of the GC-MS. The estimated error were with the T-Student method at a 95% confidence interval, for each compound at different operating conditions.
Table 4.3: Quantification of liquid samples using a laboratory scale TBR

<table>
<thead>
<tr>
<th>Compounds</th>
<th>R1 %w/w</th>
<th>R2 %w/w</th>
<th>R3 %w/w</th>
<th>R4 %w/w</th>
<th>R5 %w/w</th>
<th>R6 %w/w</th>
<th>R7 %w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>C9</td>
<td>0.03 ±0.00</td>
<td>0.03±0.01</td>
<td>0.06±0.01</td>
<td>0.04±0.01</td>
<td>0.06±0.01</td>
<td>0.04±0.01</td>
<td>0.10±0.01</td>
</tr>
<tr>
<td>C10</td>
<td>0.03±0.00</td>
<td>0.03±0.01</td>
<td>0.05±0.01</td>
<td>0.05±0.02</td>
<td>0.06±0.01</td>
<td>0.05±0.02</td>
<td>0.10±0.01</td>
</tr>
<tr>
<td>C11</td>
<td>0.10±0.05</td>
<td>0.11±0.02</td>
<td>0.20±0.01</td>
<td>0.15±0.04</td>
<td>0.21±0.01</td>
<td>0.14±0.02</td>
<td>0.18±0.02</td>
</tr>
<tr>
<td>C12</td>
<td>0.14±0.03</td>
<td>0.13±0.02</td>
<td>0.15±0.02</td>
<td>0.18±0.02</td>
<td>0.16±0.03</td>
<td>0.18±0.02</td>
<td>0.24±0.04</td>
</tr>
<tr>
<td>C13</td>
<td>0.30±0.18</td>
<td>0.33±0.07</td>
<td>0.60±0.07</td>
<td>0.47±0.10</td>
<td>0.61±0.11</td>
<td>0.42±0.01</td>
<td>0.42±0.06</td>
</tr>
<tr>
<td>C14</td>
<td>0.45±0.12</td>
<td>0.41±0.06</td>
<td>0.45±0.04</td>
<td>0.58±0.05</td>
<td>0.44±0.10</td>
<td>0.58±0.02</td>
<td>0.68±0.13</td>
</tr>
<tr>
<td>C15</td>
<td>12.73±3.94</td>
<td>13.43±3.13</td>
<td>25.37±2.97</td>
<td>19.92±4.33</td>
<td>24.99±5.55</td>
<td>17.49±1.10</td>
<td>16.26±2.54</td>
</tr>
<tr>
<td>C16</td>
<td>17.72±2.53</td>
<td>15.45±4.44</td>
<td>16.93±2.12</td>
<td>22.64±1.93</td>
<td>15.40±4.59</td>
<td>22.66±1.88</td>
<td>25.55±5.36</td>
</tr>
<tr>
<td>C17</td>
<td>16.63±5.15</td>
<td>17.39±4.89</td>
<td>32.63±4.16</td>
<td>26.19±6.01</td>
<td>32.22±6.72</td>
<td>23.41±0.44</td>
<td>22.68±3.39</td>
</tr>
<tr>
<td>C18</td>
<td>21.50±3.32</td>
<td>18.26±5.35</td>
<td>20.29±2.33</td>
<td>27.41±2.53</td>
<td>17.78±6.00</td>
<td>26.97±1.10</td>
<td>32.34±6.67</td>
</tr>
<tr>
<td>C19</td>
<td>0.23±0.09</td>
<td>0.22±0.06</td>
<td>0.40±0.05</td>
<td>0.34±0.08</td>
<td>0.36±0.05</td>
<td>0.32±0.02</td>
<td>0.37±0.05</td>
</tr>
<tr>
<td>Palmitic Acid</td>
<td>1.64±0.23</td>
<td>2.79±1.07</td>
<td>0.00</td>
<td>0.31±0.04</td>
<td>1.07±0.20</td>
<td>1.56±0.88</td>
<td>0.42±0.27</td>
</tr>
<tr>
<td>C20</td>
<td>0.22±0.03</td>
<td>0.20±0.06</td>
<td>0.20±0.02</td>
<td>0.28±0.03</td>
<td>0.19±0.06</td>
<td>0.28±0.03</td>
<td>0.33±0.06</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>0.56±0.03</td>
<td>0.92±0.037</td>
<td>0.00</td>
<td>0.09±0.14</td>
<td>0.25±0.05</td>
<td>0.55±0.26</td>
<td>0.13±0.09</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>0.70±0.22</td>
<td>1.48±0.55</td>
<td>0.00</td>
<td>0.16±0.10</td>
<td>0.68±0.20</td>
<td>0.74±0.40</td>
<td>0.22±0.09</td>
</tr>
<tr>
<td>TOTAL</td>
<td>72.97</td>
<td>71.17</td>
<td>97.32</td>
<td>98.81</td>
<td>94.49</td>
<td>95.65</td>
<td>100.00</td>
</tr>
<tr>
<td>C15-C18</td>
<td>68.58</td>
<td>64.51</td>
<td>95.21</td>
<td>96.16</td>
<td>90.39</td>
<td>90.78</td>
<td>96.83</td>
</tr>
</tbody>
</table>

Assuming that triglycerides have a reaction pathway according to section 2.2 a first approach of RBDPO hydrotreatment pathway was proposed. The proposed reaction steps such as saturation of triglycerides, production of fatty acids, hydrodeoxygenation (production of C10, C12, C14 C16, C18 and C20) and hydrodecarboxylation (production of C9, C11, C13, C15, C17 and C19). C9-10 hydrocarbons are coming from capric fatty acid chain in accordance to the oils composition in should not be possible to obtain such hydrocarbons, however low concentrations C9-C10 were gained. C11-12 hydrocarbons are coming from Lauric fatty acid chain. C13-14 hydrocarbons are coming from myristic fatty acid chain. C15-16 are coming from palmitic fatty acid chain, C17-18 are coming from stearic fatty acid chain, C19-C20 is coming from arachidic fatty acid chain. The odd-carbon chains originate from triglycerides hydrodecarboxylation and
the even-carbon chain from hydrodeoxygenation reactions. The results showed a preference to reactions of hydrodeoxygenation, due to the proportion of even hydrocarbons chains compared with the odd chains. A higher quantity of a hydrogen dissolution promotes hydrodeoxygenation reactions, also the selectivity of these reactions depends on reactor conditions and the catalyst. The hydrodeoxygenation is also favored by high temperatures and high liquid space velocity LHSV [52].

Figure 4.4 shows bar graphs that summarizes the results in Table 4.3 depending on liquid residence time, temperature and pressure respectively. The main identified compounds are C15-C18. The total concentration increases with the operating conditions as was expected but is the compounds are analyzed separately it is observed maximums or minimums in the bars for these alkanes production due to competence of hydrodeoxygenation and hydrodecarboxylation as reported others authors [19, 29, 49, 51, 59].
4.2 Results and discussion

**Figure 4.4:** Variation of the concentration of C15-C18 alkanes and others (C9-C19,C19-C20 and fatty acids) with: a) Liquid residense time at 350°C and 60 bar b) Temperature at 60 bar and \( \tau \) equal to 30 min c) Pressure at 350°C and \( \tau \) equal to 30 min
Due to in the continuous were identified more compounds than in semi-batch setup was necessary to propose additional reaction that in Table 3.4. Table 4.4 shows the conditional reactions that describes the HDT of RBDPO. This reactions was proposed considering hydrodeoxygenation and hydrodecarboxylation reactions of trilaurin and hydrodeoxygenation of triarachidin according to section 2.2.

Table 4.4: Additional reactions for RBDPO hydrogenation for the proposed pathway

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction Type</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R18</td>
<td>Hydrodeoxygenation</td>
<td>$C_{39}H_{74}O_6 + 12H_2 \rightarrow 3C_{12}H_{26} + C_3H_8 + 6H_2O$</td>
</tr>
<tr>
<td>R19</td>
<td>Hydrodeoxygenation</td>
<td>$C_{63}H_{122}O_6 + 12H_2 \rightarrow 3C_{20}H_{42} + C_3H_8 + 6H_2O$</td>
</tr>
<tr>
<td>R20</td>
<td>Hydrodecarboxylation</td>
<td>$C_{39}H_{74}O_6 + 3H_2 \rightarrow 3C_{11}H_{34} + C_3H_8 + 3CO_2$</td>
</tr>
</tbody>
</table>

4.2.2. Kinetic analysis

Due to mathematical complexity that the evaluation of 40 kinetic parameters would impose, a simplified reaction pathway with lower number of reactions that than in Table 3.4 and 4.4 was developed. Table 3.1 shows that triolein (OOO), trilinolein (LLL), tripalmitin (PPP) and tristearin (SSS), account for 95% of the composition of RBDPO. It is, therefore, reasonable to propose a simplified composition of the RBDPO for the kinetic analysis. A simple normalization of the concentration of these species yields the following composition: oleic 41.09%w, palmitic 36.53%w, linoleic 13.81%w and stearic 8.57%w. Furthermore, Table 4.3 indicates that the concentration of C15-C18 hydrocarbons represents over 95% of the identified liquid products and between 65% and 97%, depending on the reaction conditions, of the total liquid production. Following the simplification of only considering major-concentration species as reactants, it seems possible to simplify the products for the kinetic analysis as hydrocarbons C15 to C18. This is clearly a simplification imposed by the multiple reactions and the few data points that the experimental campaign was able to produce.

More difficult that the simplification of the number of reactants and products is the reduction of the number of reactions in the system. Table 4.5 shows the reduced reaction pathway that only considers six reactions: hydrogenation of trilinolein and triolein to produce triestearin. The two surviving triglycerides, tripalmitin and triestearin (both, originally present in the oil or produced by the hydrogenation reactions) undergo hydrodeoxygenation and hydrodecarboxylation reactions that produce the C15 to C18. This six
reaction was simulated in ASPEN PLUS V8.4 to estimate the reaction heat. It is observed that all the reactions are exothermic.

Table 4.5: Simplified HVO pathway used for the estimation of the kinetic parameters

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction Expression</th>
<th>Kinetic Expression</th>
<th>Reaction Heat [kJ/mol – H₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>( \text{C}<em>{57}\text{H}</em>{98}\text{O}<em>6 ) + 6( \text{H}<em>2 ) → ( \text{C}</em>{57}\text{H}</em>{110}\text{O}_6 )</td>
<td>( r'<em>1 = k_1\text{C}</em>{\text{OOO}} )</td>
<td>-82.64</td>
</tr>
<tr>
<td>R2</td>
<td>( \text{C}<em>{57}\text{H}</em>{110}\text{O}<em>6 ) + 3( \text{H}<em>2 ) → ( \text{C}</em>{57}\text{H}</em>{110}\text{O}_6 )</td>
<td>( r'<em>2 = k_2\text{C}</em>{\text{LLL}} )</td>
<td>-39.24</td>
</tr>
</tbody>
</table>

Hydrodeoxygenation

| R3              | \( \text{C}_{51}\text{H}_{98}\text{O}_6 \) + 12\( \text{H}_2 \) → \( 3\text{C}_{16}\text{H}_{34} + \text{C}_3\text{H}_8 + 6\text{H}_2\text{O} \) | \( r'_3 = k_3\text{C}_{\text{PPP}} \) | -65.17 |
| R4              | \( \text{C}_{57}\text{H}_{110}\text{O}_6 \) + 3\( \text{H}_2 \) → \( 3\text{C}_{18}\text{H}_{38} + \text{C}_3\text{H}_8 + 6\text{H}_2\text{O} \) | \( r'_4 = k_4\text{C}_{\text{SSS}} \) | -68.82 |

Hydrodecarboxylation

| R5              | \( \text{C}_{51}\text{H}_{98}\text{O}_6 \) + 3\( \text{H}_2 \) → \( 3\text{C}_{15}\text{H}_{32} + \text{C}_3\text{H}_8 + 3\text{CO}_2 \) | \( r'_5 = k_5\text{C}_{\text{PPP}} \) | -99.95 |
| R6              | \( \text{C}_{57}\text{H}_{110}\text{O}_6 \) + 3\( \text{H}_2 \) → \( 3\text{C}_{17}\text{H}_{36} + \text{C}_3\text{H}_8 + 3\text{CO}_2 \) | \( r'_6 = k_6\text{C}_{\text{SSS}} \) | -111.61 |

The kinetic expressions for each proposed reaction was assume to be first order with respect to each triglyceride molecule as Sebos et al. [40]. Equations \( r'_1 \) to \( r'_6 \) from Table 4.5 are the proposed kinetics expressions for the reduced reaction pathway of RBDPO hydrotreatment. Assuming that the reactions rate follows an Arrhenius law, a total of six pairs of activation energies and frequency factors need to be determined in the system. These parameters were optimized using MatLab subroutine that applies an unconstrained nonlinear minimization. The model only considers temperature and liquid residence time. These variables are related in the model to the reaction constant and the total volumetric flow. The model does not include the total system pressure as it neglects any mass transfer restrictions and the reaction rates only involve the concentration of triglycerides. This approximations would be valid in the case were the hydrogen concentration in the liquid phase would be high enough so that the kinetic reaction of hydrogen with the glycerides would be the limiting step. The fact that the experiments suggest that there is a very low dependence of the final product composition on pressure supports this assumption. Assuming
plug flow though the reactor, the general differential equation for the laboratory-scale HDT reactor for \( i \) component is Equation 4.1.

\[
\frac{dC_i}{dL} = \frac{A\rho_{\text{bulk}}}{v_o} r_i'
\]  
(4.1)

where:

\( r'_{LLL} = -r_1' \)
\( r'_{OOO} = -r_2' \)
\( r'_{SSS} = r_1' + r_2' - r_4' - r_6' \)
\( r'_{PPP} = -r_4' - r_6' \)
\( r'_{C16} = 3r_3' \)
\( r'_{C18} = 3r_4' \)
\( r'_{C15} = 3r_5' \)
\( r'_{C17} = 3r_6' \)

\( C \): Concentration, (\( kmol/mm^3 \))
\( \rho_{\text{bulk}} \): Catalyst bulk density, (kg/m\(^3\))
\( A \): Reactor cross section (m\(^2\))
\( v_o \): Total volumetric flow, RBDPO plus hydrogen flow (m\(^3\)/h)
\( L \): Reactor length (m)

To conduct the optimization, it is necessary to normalize the triglycerides original concentration (in \( \%w/w \) in Table 3.1) to obtain \( kmol/m^3 \) as required by the model (Equation 4.1). Equation 4.2 shows the normalization procedure.

\[
C_{\text{Triglyceride}} = Normalized\%w/w \times \frac{\rho_{\text{Triglyceride}} \times v_{o,i}}{MW_{\text{Triglyceride}} \times v_o}
\]  
(4.2)

where:

\( \rho_{\text{Triglyceride}} \): Triglyceride density, (kg/m\(^3\))
\( v_{o,i} \): Inlet RBDPO volumetric flow, (m\(^3\))
4.2 Results and discussion

$MW_{\text{Triglyceride}}$: Triglyceride molecular weight, (kg/kmol)

$v_o$: Inlet volumetric flow, RBDPO plus hydrogen flow, ($m^3/h$)

In the analysis the initial concentration for alkanes C15-C18 was assumed as zero and the final concentration are in Table 4.3, was converted from %w/w of the liquid sample to total kmol/m$^3$ based on the original triglyceride input to the reactor, as explained in Equation 4.3:

$$C_{\text{Alkane}} = \frac{\%w/w \times \rho_{\text{Alkane}} \times v_{o,\text{out}}}{MW_{\text{Alkane}} \times v_{\text{out}}}$$  \hspace{1cm} (4.3)

where:

$\rho_{\text{Alkane}}$: Alkane density, (kg/m$^3$)

$v_{o,\text{out}}$: Outlet Alkane volumetric flow ($m^3$)

$MW_{\text{Alkane}}$: Triglyceride molecular weight (kg/kmol)

$v_{\text{out}}$: Outlet volumetric flow, alkane plus gaseous phase flow ($m^3/h$)

$v_{o,i}$ and hydrogen flow were taken according with the operating conditions in Table 5.2. $v_{o,\text{out}}$ was measured when the liquid phase was sampled and the liquid sample was brought to analysis, the outlet gaseous volumetric flow was assumed equal to the inlet hydrogen flow as the total reaction gas product flow was negligible when compared to the hydrogen flow.

The objective function for the optimization process was the mean square error, MSE in Equation 4.4 between experimental observations and model prediction.

$$MSE = \frac{\sum_{i=1}^{n} (C_{i}^{\text{exp}} - C_{i}^{\text{pred}})^2}{2}$$  \hspace{1cm} (4.4)

where $n$ is the number of observations equals to twenty (four alkanes C15-C18 concentration at five operating conditions), and $C_{i}^{\text{exp}}$ and $C_{i}^{\text{pred}}$ are the experimental and predicted concentration of the liquid identified compounds respectively.
Table 4.6 presents the optimized kinetic parameters. While the values of the parameters in Table 4.6 result from fitting the experimental data to a rather empirical model, the fact that the values of the activation are in the expected range for a chemically-controlled reaction give confidence in the model.

<table>
<thead>
<tr>
<th>$E_a$ [kJ/kmol]</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>
</tr>
</thead>
<tbody>
<tr>
<td>149.9</td>
<td>162.5</td>
<td>147.4</td>
<td>149.1</td>
<td>150.6</td>
<td>169.2</td>
<td></td>
</tr>
</tbody>
</table>

$\kappa_0 [1/s] = 9.4 \times 10^{11}$  $4.4 \times 10^{13}$  $3.8 \times 10^{10}$  $5.6 \times 10^{10}$  $1.4 \times 10^{10}$  $8.2 \times 10^{11}$

Figure 4.5 and 4.6 show the variation of the concentration alkanes C15, C16, C17, C18 with temperature and liquid residence time and temperature respectively from the experiments and as predicted by the model with the optimized parameters. The experimental results show a subtle increase in hydrocarbon concentration as temperature and residence time increase. However, some cases present a maximum in the intermediate temperature or the intermediate residence time that may be associated to competition between the hydrodeoxygenation and hydrodecarboxylation reactions at the operating conditions of this thesis, something that has also been observed by previous studies [19, 29, 49, 51, 59]. While the model captures the general trend of the experiments, in some cases, fails to predict the maxima at intermediates conditions. Clearly the simplifications explained above yield a model that needs to be improved in order to capture the complete hydrogenation process. Nevertheless, the model was considered as a good first-order approximation for the design of the hydrogenation reactor that was the main objective of this thesis.
4.2 Results and discussion

**Figure 4.5:** Comparison of the variation of the concentration with temperature as predicted with the model and the experimental result. a) C15, b) C16, c) C17, d) C18

**Figure 4.6:** Comparison of the variation of the concentration with RBDPO residence time as predicted with the model and the experimental result. a) C15, b) C16, c) C17, d) C18
Table 4.7 presents the concentration as predicted by the proposed kinetic model and the experimental value for different temperatures and liquid residence times considered in this study. Figure 4.7 shows the parity plot for experimental and predicted values. The value of the correlation coefficient in Figure 4.7 ($R^2 = 0.80$) as well as a review of the values in Table 4.7 confirm the results in Figure 4.5 and 4.6. While there is in general good agreement between experiments and the model, the last one fails to predict some intermediate values. There is clearly a shortcoming in the model that needs to be corrected in future research. Nevertheless, the current version should give the first order estimate of the dimensions required for the reactor design that is explained in the next chapter.

Table 4.7: Calculated and experimental (in parenthesis) concentration for the different hydrocarbons. The model considered the proposed reaction mechanism for RBDPO hydrogenation. The results are presented for the conditions described in Table 4.1.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (Experiments) [kmol/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1</td>
</tr>
<tr>
<td>C15</td>
<td>0.031(0.028)</td>
</tr>
<tr>
<td>C16</td>
<td>0.033(0.037)</td>
</tr>
<tr>
<td>C17</td>
<td>0.037(0.033)</td>
</tr>
<tr>
<td>C18</td>
<td>0.033(0.040)</td>
</tr>
</tbody>
</table>
4.3 Summary

The continuous reaction of hydrogenation of RBDPO in a laboratory-scale TBR was successfully carried out as the significant production of alkanes. The reaction mechanism proposed in the previous chapter was updated with some reactions that were evident in the continuous reactor because the conversion in this reactor was higher than in the batch reactor. The new mechanism includes 18 reactions and 27 species. Obtaining values for all the kinetic parameters for this mechanism is a very difficult process and is impossible with the limited experimental data available for this research. However, a simplified kinetics mechanism was developed. This reduced reaction mechanism took advantage of the fact that most of the products were hydrocarbons in the C15 to C18 range. Estimation of the kinetic parameters based on the experimental data allowed for a good prediction of the experimental data. Nevertheless, some data points for hydrocarbon concentration, particularly at intermediate conditions, were underestimated by the model. While clearly the model needs improvements in order to correctly capture all the experimental trends, the combination of experiments and reduced mechanisms can give a first order estimate of the reactor setup that may have applications for the industrial conversion of RBDPO into diesel.

Figure 4.7: Parity plot of the predicted and experimental concentration of hydrocarbons for the TBR experimental setup, \( R^2 = 0.80 \)
Chapter 5

Reactor design

This chapter details the methodology followed to carry out a conceptually design of a hydrotreatment reactor with a production typical of an industrial unit. The chapter includes the procedure followed to estimate the thermophysical properties of the feedstock and the operating conditions and size of the proposed reactor. Additionally, two case studies are used to illustrate the design process.

5.1. Modeling

Following the thesis structure that was outlined in the previous chapters, the first part of this chapter describes the methodology used to have a conceptual design of the hydrogenation reactor.

5.1.1. Balance model of the hydrotreatment reactor

This research assumed that a TBR could be considered a PBR which has much simpler mathematical description. Deviations from ideal plug flow were neglected because of the low liquid velocity. PBR assumes that all the volume elements in the reactor have the same space time, to have the same contribution to conversion and identical wet catalyst area. The PBR mole balance in the design of the reactor was:

\[
\frac{dF_i}{dW} = r'_i
\]

where:

- \( C_i \): Concentration of species \( i \), (kmol/m\(^3\))
- \( v_o \): Total volumetric flow, (m\(^3\))
5.1 Modeling

$r'_i$: Reaction rate of species $i$ per unit of catalyst, (kmol/kg catalyst-s)

$F_i = C_i/v_o$: Molar flow of species $i$ kmol/s

$dW = \rho_{bulk}dV = \rho_{bulk}AdL$

$\rho_{bulk}$: Catalyst bulk density, (kg/m$^3$)

A: Reactor cross section, $m^2$

L: Reactor long, $m$

Reordering and replacing terms yields expression 5.2 which was the one used in the model

$$\frac{dC_i}{dL} = \frac{A\rho_{bulk}v_o}{v_o}r'_i$$

The kinetics mechanism used for industrial reactor design was the purpose in Table 4.5. The energy balance was calculated with Equation 5.3 correspond temperature variation of PBR. The overall heat-transfer coefficient 4962 W/m$^2$ - K was taken from master thesis [58] (a CFD study of the heat transfer in a hydrotreatment reactor). The catalyst used for the industrial reactor design was the same that experimental work.

$$\frac{dT}{dW} = \frac{U_a(T_a - T) + \sum_{i=1}^{q}(r_{ij})[\Delta H_{Rxij(T)}]}{\sum_{j=1}^{m}F_jC_{pj}}$$

where:

$U$: Overall heat-transfer coefficient, (W/m$^2$ - K)

$a$: PFR heat-exchange area per volume of reactor, (m$^2$/m$^3$)

$H_{Rxij(T)}$: heat of reaction with respect to species $j$ in reaction $i$, (J/mol)

$T_a$: Thermal fluid temperature (kg/m - s)

$C_{pj}$: Heat capacity of species $j$, (J/mol - K)

The pressure drop was calculated with Ergun Equation 5.4 of packed bed.

$$\frac{dP}{dz} = -\frac{G}{\rho d_p} \left(1 - \phi \right) \left[ \frac{150(1 - \phi)\mu}{d_p} + 1.75G \right]$$
where:

- \( P \): Pressure, \( (kPa) \)
- \( \phi \): Porosity
- \( d_p \): Diameter of Particle, \( (m) \)
- \( \mu \): Gas viscosity, \( (kg/m \cdot s) \)
- \( L \): Reactor long, \( (m) \)
- \( G \): Gas Flux, \( (kg/m^2 \cdot s) \)
- \( \rho_{bulk} \): Catalyst bulk density, \( (kg/m^3) \)
- \( A \): Reactor cross section, \( m^2 \)

### 5.1.2. Thermophysical Properties

To develop a phenomenological model to design a reactor was necessary to estimate the thermophysical properties of the feedstock, intermediates and products in the reaction process, therefore, it was developed a components property database. To estimate triglycerides properties it was necessary applying a group contribution method as Zong et al. [60], this method corresponded within less than 10% of error. Table 5.1 shows the equations to estimate the molar volume, heat capacity and viscosity in liquid phase of triglycerides. The terms \( V_{A}^{l}, C_{P,A}^{l} \) and \( \mu^{l} \) was taken from [60]. The database of estimated properties of triglycerides was applied to this work. For the others species (alkanes and gases) ASPEN PLUS V8.4 database was used.
Table 5.1: Properties group contribution method equations for liquid molar volume, heat capacity and viscosity of triglycerides

<table>
<thead>
<tr>
<th>Triglycerides properties</th>
<th>Liquid molar volume</th>
<th>Liquid heat capacity</th>
<th>Liquid viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V^l = N_{frag} \sum_A^N x_A V^l_A(T)$</td>
<td>$C^l_P = N_{frag} \sum_A^N x_A C^l_{P,A}(T)$</td>
<td>$\ln \mu^l = N_{frag} \sum_A^N x_A \ln \mu^l_A(T)$</td>
</tr>
</tbody>
</table>

where:

- $N_{frag}$: Number of fragments in the triglyceride
- $x_A$: Mole fraction of fragment A in the triglyceride
- $V^l_A$: Liquid molar volume of fragment A in the triglyceride for temperature dependency, $(m^3/kmol)$
- $C^l_{P,A}$: Liquid heat capacity of fragment A in the triglyceride for temperature dependency, $(J/kmol-K)$
- $\mu^l$: Liquid viscosity of fragment A in the triglyceride for temperature dependency, $(Pa-s)$

The development of cases study was conducted according with the algorithm proposed in Figure 5.1. The algorithm considered mainly parameters for the design such as reactor diameter, thermal fluid temperature, hydrogen quenching flow and maximum temperature inside the reactor below $370^\circ C$.

![Figure 5.1: Proposed algorithm for the two cases study that consider the design of an industrial reactor](image)

The solution of the model, was carried out using the ASPEN PLUS V8.4 commercial software simulator. Was solved the balance of mole, energy and Ergun equations to obtain temperature, species flow molar and pressure profiles in the hydrotreating reactor.
5.2. Results and discussion

5.2.1. Operating conditions, feedstock and reactor dimensioning

Fedepalma, the organization responsible for palm oil production Colombia reports close to 940.8×10^3 tonnes per year of crude palm oil production [4]. This research aimed at designing a reactor with the capacity to hydrogenate 10% of Colombia’s palm oil production because the rest of RBDPO production is destined for food, cosmetic and transesterification industry. The hydrogen flow was calculated using $H_2/\text{RBDPO} = 20$ molar ratio. The kinetic data was estimated at constant pressure of 60 bar, therefore, that pressure inlet was proposed. Also it was selected high conversion of triglycerides 1 and 0.97 for tripalmitin and tristearin, respectively, the tripalmitin has higher reaction rate than tristearin due to that tripalmitin does not need saturation reaction while the tristearin have saturation reactions of triolein and trilinolein. Table 5.2 summarizes the feedstock conditions for the design of an industrial-size reactor.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$ Mass flow</td>
<td>59 kg/h</td>
</tr>
<tr>
<td>RBDPO Mass flow</td>
<td>1251 kg/h</td>
</tr>
<tr>
<td>Inlet Pressure</td>
<td>60 bar</td>
</tr>
</tbody>
</table>

5.2.2. Cases study of reactor design proposed

This section presents the results of simulations of two cases of study for the industrial reactor design. Given the high exothermicity of the reaction, the design took special consideration to prevent the formation of hot spots in the reactor. To prevent cracking of the hydrocarbons, but maintain an active reaction rate, the reactor was designed to maintain a temperature below 370°C. Hence the temperature inside the reactor was considered a critical parameter for the design, as also were the energy released per reaction and the of reaction progress. The choice of the last or these variables is obvious as the objective of an industrial reactor is to maximize hydrocarbon production. Studying the variation of the energy produced by each reaction is fundamental for the understanding of the reaction process, as illustrated below.
5.2 Results and discussion

5.2.3. Case study 1

This analysis considered that the RBDPO inlet temperature into the reactor was at least of $65^\circ C$ taking account that at temperatures below $45^\circ C$ the RBDPO has semi-solid behavior. The reactor diameter was selected as 0.65 m based on $L/D = 1.6$ [58] and a maximum catalyst bed height of 1 m as recommended by the manufacturer. The thermal fluid temperature $T_a = 346^\circ C$ was selected according to the maximum temperature allowed in the reactor ($T_{max} = 370^\circ C$). Table 5.3 shows the dimension and operation conditions of case study 1. Figure 5.2 shows the industrial reactor scheme for case study 1 to produce renewable diesel from RBDPO. Figure 5.2 shows a scheme of the reactor setup selected for Case 1. Both hydrogen and RBDPO enter the reactor from the top.

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>0.625 m</td>
</tr>
<tr>
<td>Bed length</td>
<td>10.15 m</td>
</tr>
<tr>
<td>Thermal fluid temperature</td>
<td>$346^\circ C$</td>
</tr>
<tr>
<td>PPP conversion</td>
<td>1</td>
</tr>
<tr>
<td>SSS conversion</td>
<td>0.97</td>
</tr>
<tr>
<td>Flow pattern</td>
<td>Trickle flow</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>0.1 bar</td>
</tr>
<tr>
<td>Heat duty</td>
<td>54.84 kW</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>2232 kg</td>
</tr>
<tr>
<td>Catalyst volume</td>
<td>3.11 $m^3$</td>
</tr>
</tbody>
</table>
Figure 5.2: Scheme of the proposed setup for the reactor for Case 1

Figure 5.3 a) shows the temperature profile inside the reactor. The simulation shows a maximum temperature of 369.6°C at 55 cm, then a reduction due to heat exchange with the thermal fluid. Figure 5.3 b) shows that the pressure drop, calculated by Ergun equation is negligible.
5.2 Results and discussion

The increase in temperature in the reactor could be understood based on the analysis of the energy released by every reaction in the mechanism in Table 4.5. Figure 5.4 shows that all reactions present a peak in the energy released close to 0.55 m that agrees with the maximum in temperature observed in Figure 5.2a. The reactions that present a most significant contribution to this peak are number three and four. However, all reactions contribute to the rapid increase in temperature. While energy production by all reactions is significant along the reactor, it tends to be negligible beyond beyond 5 m. It is also evident that the role of the heat transfer fluid is to prevent that in the first part of the reactor the temperature surpasses the limit of 370°C and that, in the last part of the reactor, the temperature remains high-enough to achieve a high conversion.
Figure 5.4: Energy released along the reactor by reactions: a) R1, b) R2, c) R3, d) R4, e) R5, and f) R6. See Table 4.5 for a complete description of the reactions.
5.2 Results and discussion

Figure 5.5 shows the molar flow of all triglycerides (OOO, LLL, SSS and PPP) along the reactor. The simulation suggests that triolein and trilinolein rapidly hydrogenize to for triestearin. The reaction of triestearin and tripalmitin to form hydrocarbons proceeds at a much lower rate and explains the need for a reactor longer than 10 m.

Figure 5.5: Predicted molar flow of triglycerides along the reactor for Case 1: a) Triolein OOO, b) Trilinolein LLL, c) Tristearin SSS, d) Tripalmitin PPP

Figure 5.6 shows the molar flow of alkanes (C15, C16, C17, C18). At the beginning of the reactor the production of alkanes is low, probably because the temperature in the reactor is too low. However, at 5 m the triglyceride (PPP) has a conversion of 97% to C15-C16 this length the conversion of SSS is only 82%. A reactor length of 10.15 m is required to obtain 97% conversion of SSS.
5.2.4. Case study 2

A reactor design was considered with the RBDPO inlet temperature of 65°C and a thermal fluid temperature of 355°C higher than Case 1. It is worth noting that if the thermal fluid temperature is increased a hot-spot could be formed too close of the top of the reactor, and if the reactor diameter is maintained than in case 1 the hot-spot could be formed before 55 cm of the top of the reactor, therefore the diameter of the reactor was also decreased to improve heat transfer from the thermal fluid and displace the hot-spot. The minimum distance of hydrogen quenching was established at 55 cm from the top of the reactor. Table 5.4 shows the dimension and operating conditions of the reactor of case study 2. Figure 5.7 shows
the proposed reactor setup that considers hydrogen quenching to address the temperature peak observed at 58 cm in Case 1.

![Industrial TBR scheme](image)

**Figure 5.7**: Industrial TBR scheme

**Table 5.4**: Industrial reactor dimensioning for case study 2

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>0.4 m</td>
</tr>
<tr>
<td>Location of hydrogen quench</td>
<td>0.58 m</td>
</tr>
<tr>
<td>Bed Length</td>
<td>16.3 m</td>
</tr>
<tr>
<td>Thermal fluid temperature</td>
<td>355°C</td>
</tr>
<tr>
<td>PPP conversion</td>
<td>1</td>
</tr>
<tr>
<td>SSS conversion</td>
<td>0.97</td>
</tr>
<tr>
<td>Flow pattern</td>
<td>Trickle flow</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>0.6 bar</td>
</tr>
<tr>
<td>Heat duty</td>
<td>70 kW</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>1467 kg</td>
</tr>
<tr>
<td>Catalyst volume</td>
<td>2.05 $m^3$</td>
</tr>
</tbody>
</table>
Figure 5.8a) shows the temperature profile inside the reactor. Before hydrogen quench in blue and after the quench in red, the simulation shows a maximum in temperature around 58 cm. The hydrogen quench decreases the temperature which increases again but does not become higher than 370°C as the heat exchange with the thermal medium prevents such undesirable outcome. Figure 5.8 b) Shows that the pressure drop is very low but significantly higher than the one calculated for Case 1.

![Figure 5.8: a) Temperature profile and b) Pressure drop in the reactor](image)

Figure 5.9 shows the energy released by each reaction. While the results are similar to those obtained for Case 1, in Case 2 it is evident that the injection of $H_2$ decreases the rate of heat release to values comparable to those in Case 2. Nevertheless, in some cases the rate of heat release before quenching is higher than that for Case 1.
Figure 5.9: Energy released along the reactor for Case 2 by reactions: a) R1, b) R2, c) R3, d) R4, e) R5, and f) R6. See Table 4.5 for a complete description of the reactions.
Figure 5.10 shows the molar flow of triglycerides OOO, LLL, SSS, PPP. OOO and LLL are consumed mainly before hydrogen quenching. The molar flow of SSS increases due to triglyceride saturation reactions mainly before hydrogen quenching and decreases by the formation of alkanes product of hydrodeoxygenation and hydrodecarboxylation.

**Figure 5.10:** Predicted molar flow of triglycerides along the reactor for Case 2: a) Triolein OOO, b) Trilinolein LLL, c) Tristearin SSS, d) Tripalmitin PPP

Figure 5.11 shows the mole flow of alkanes C15, C16, C17, C18. The trends are similar to those observed for Case 1. The main difference is that a significant production of hydrocarbons is obtained at higher lengths of the reactor as was expected given the lower diameter in Case 2.
Figure 5.11: Predicted molar flow of alkanes along the reactor for Case 2: a) C15, b) C16, c) C17, d) C18

Figure 5.12 shows the alcanes-RBDPO mass flow ratio for the reactors designs. Case 2 reaches an ALKANES/RBDPO ratio close to 0.8 with lower catalyst load than Case 1, therefore a reactor operating at a temperature of thermal flow at 355°C and at 60 atm with 1467 kg can convert 10% of the Colombian production of RBDPO to hydrocarbons.
5.3. Summary

Two case studies that attempt to propose a possible conceptual design of the reactor were presented in this section. The main emphasis in design was to guarantee that the reactor did not present any hot spots and particularly that the temperature does not exceed 370°C to prevent cracking of products and to operate within the catalyst operation temperature range. An analysis of two case studies where two reactor configurations were simulated using the software ASPEN PLUS 8.4 was carried out taking special care to construct a comprehensive database of reactants and intermediate product’s thermophysical properties. The first case considered the injection of hydrogen at the top of the reactor concurrently with the RBDPO. The inlet temperature and that of the heating fluid were selected to prevent formation of hotspots and guarantee adequate conversion in the reactor. The second case was similar to the first one except for the injection of hydrogen 58 cm from the top of the reactor. For the second case a low reactor diameter was proposed for the design to improve heat exchange. Both cases present the same conversions at different operating conditions but due to a lower catalyst weight (765 kg less), smaller reactor’s (1 $m^3$ less), the reactor design in Case study 2, is a better option for and industrial application.
Conclusions

A successful RBDPO hydrogenation was carried out in a semi-batch reactor. The low conversion to hydrocarbons was ideal to propose a reaction pathway for the process. The main products were intermediate species such as fatty acids, monoglycerides and, probably, diglycerides. Table 3.4 presents the most probable reactions taking place in the system. After the saturation of triglycerides, they are converted to diglycerides, monoglycerides, fatty acids and alkanes through reactions of hydrogenolysis, hydrodecarboxylation and hydrodeoxygenation. The lower conversion to alkanes demonstrates that the semi-batch configuration is not the best option for RBDPO hydrogenation but the identified monoglycerides and fatty acids allow to verify the reaction pathway. A higher conversion of RBDPO triglycerides would take too much time [48, 49, 55] (3-6 h), therefore a kinetic study is not appropriate in a stirred tank semi-batch reactor. The semi-batch hydrogenation could be affected by the hydrogen mass transfer. In semi-batch configuration the hydrodecarboxylation reactions are significantly higher than hydrodeoxygenation reaction probably due to limited and poor hydrogen diffusion in the RBDPO.

To obtain a better approximation of the kinetics in the system, a laboratory-scale TBR was designed and constructed. The main products of the operation of the continuous reactor were C15-C18 paraffins and the conversion was higher than 97%. The higher conversion to alkanes demonstrates that a continuous configuration is the best option for RBDPO hydrogenation. The results of the continuous reactor that presented a higher conversion allowed for a more complete description of the reaction mechanisms as some compounds, only detectable at higher conversion where analyzed. However, the low number of data points forced the use of a simplified reaction mechanism that captured the most relevant trends of the reaction system. However, the trend of C15-C18 hydrocarbon production at some intermediate conditions were not reproduced probably due to competitions between the hydrodeoxygenation and hydrodecarboxylation reactions on the fact that they show a high dependence on catalyst selectivity, temperature, pressure and liquid residence time as reported in references [29, 49, 52]. Nevertheless, the proposed kinetics mechanism
Conclusions

was used as a first approach of RBDPO hydrotreatment kinetics for the reactor design.

The design of an industrial reactor was attempted based on two case studies. concentrated on avoiding temperatures higher than 370°C to prevent cracking and maintain the reactor in the catalyst operation temperature range. While the first case study considered concurrent injection of hydrogen and RBDPO at the top of the reactor, the second included a hydrogen-quenching stream close to the entrance of the reactor. Furthermore, the second case a low reactor diameter to improve heat exchange. Due to the lower catalyst weight, the dimensions the reactor design in the case study 2, is considered a better option for industrial application. The hydrotreatment of palm oil have a higher temperature dependence, Case 2 shows that an increase of 9°C can reduce the catalyst weight in close to 800 kg. A hydrogen quench displaces downstream the maximum temperature in the reactor. Therefore a significant reduction in the temperature profile was obtained. This thesis presented a comprehensive study of the hydrotreatment of refined palm oil. From an experimental point of view reactions in batch and continuous reactors allowed a basic understanding of the hydrotreatment process required to propose a first approximation of a reactor design. Given the complexity of the system, further work is required to improve the results here obtained. Some activities that can lead that effort are:

- To consider more complex reaction expressions not limited to first order for the reaction system.
- To explore a low-pressure regime for hydrogenation give the relatively high conversion obtained at 30 bar.
Appendix A: GC-MS analysis: peak assignments and mass spectra analysis

To determine the samples composition and characterization was necessary to realize a detailed analysis of chromatograms and mass spectrum. Only for reaction number 1, of Table 3.2, a detailed analysis is conducted. The analysis for the rest of the reactions is the same as the signals in chromatogram and mass spectrum were qualitatively the same.

Table 3.1 shows the initial RBDPO composition, organized decreasingly according with fatty acid components. The principal fatty acids were selected. Table 3.3 shows the identified components after carry out the hydrotreatment reactions. C13-14 are coming from myristic fatty acid chain, C15-16 are coming from palmitic fatty acid chain, C17-18 are coming from oleic fatty acid chain, C19 is coming from arachidic fatty acid chain. The odd carbon chain proceeds from triglycerides deoxygenation and even carbon chain from hydrodeoxygenation reaction.

The chromatogram in Figure 5.13 related to reaction 1 in Table 3.2, the using standard for these experiments was octane corresponding peak number 1. The most RBDPO composition is around C14-C18 carbon chain triglycerides so, depending of reactions of hydrodeoxygenation or hydrodecarboxylation the most possible formed alkanes are C13 - C18.
Each peak in Figure 5.13 was analyzed by the mass spectra, including the standard since retention time 0 at 50 min. Table 5.5 shows the formula and molecular weight for peak number 1.

**Table 5.5: Compound assignment of peak number 1**

<table>
<thead>
<tr>
<th>Item</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>Octane</td>
</tr>
<tr>
<td>Formula</td>
<td>$C_8H_{18}$</td>
</tr>
<tr>
<td>MW</td>
<td>114.23</td>
</tr>
</tbody>
</table>

In Figure 5.14 the experimentally determined octane mass spectrum and in Figure 5.14 the NIST database are showed, each spectrum has the biggest mass fragmentation at 40, 60, 70 and 85 and the final mass peak is at 114 m, corresponding to $C_3H_7$, $CH_2$, $CH_2$, $CH_2$ and final $C_2H_5$ fragmentation. Note that y
axis, relative intensity is not at same scale.

**Figure** 5.14: Experimental mass spectrum determined for peak number 1 assigned to octane

Now the peak at retention time 9.4 min is analyzed. **Table** 5.6 shows the formula and molecular weight for
peak number 2.

<table>
<thead>
<tr>
<th>Item</th>
<th>Assigned Compound Tridecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{13}H_{28}$</td>
</tr>
<tr>
<td>MW</td>
<td>114.23</td>
</tr>
</tbody>
</table>

In Figure 5.16 the experimentally determined tridecane mass spectrum and in Figure 5.17 the NIST database, each spectrum has the biggest mass fragmentation at 40, 60, 70, 85, 100, 120 140 and 155 the final mass peak is at 184 m, corresponding to $C_3H_7$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$ and final $C_2H_5$ fragmentation. Note that y axis, relative intensity is not at same scale.

**Figure** 5.16: Experimental mass spectrum determined for peak number 2 assigned to tridecane
Now the peak at retention time 12 min is analyzed. Table 5.7 shows the formula and molecular weight for peak number 3.

<table>
<thead>
<tr>
<th>Item</th>
<th>Tetradecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>$C_{14}H_{30}$</td>
</tr>
<tr>
<td>Formula</td>
<td>$C_{14}H_{30}$</td>
</tr>
<tr>
<td>MW</td>
<td>198.39</td>
</tr>
</tbody>
</table>

In Figure 5.17 the NIST database tridecane mass spectrum is shown.

In Figure 5.18 the experimentally determined tetradecane mass spectrum and in Figure 5.19 the NIST database, each spectrum has the biggest mass fragmentation at 40, 60, 70, 85, 100, 113, 127, 140 and 155 the final mass peak is at 198 m, corresponding to $C_3H_7$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, and final $C_2H_5$ fragmentation. Note that y axis, relative intensity is not at same scale.
Figure 5.18: Experimental mass spectrum determined for peak number 3 assigned to tetradecane

Figure 5.19: NIST database tetradecane mass spectrum

Now the peak at retention time 14.7 min is analyzed. Table 5.8 shows the formula and molecular weight for peak number 4.
Table 5.8: Compound assignment of peak number 4

<table>
<thead>
<tr>
<th>Item</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>Pentadecane</td>
</tr>
<tr>
<td>Formula</td>
<td>$C_{15}H_{32}$</td>
</tr>
<tr>
<td>MW</td>
<td>212.41</td>
</tr>
</tbody>
</table>

In Figure 5.20 the experimentally determined tetradecane mass spectrum and in Figure 5.21 the NIST database, each spectrum has the biggest mass fragmentation at 40, 60, 70, 85, 100, 113, 127, 140, 155, 169 and 183 the final mass peak is at 212 m, corresponding to $C_3H_7$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, and final $C_2H_5$ fragmentation. Note that y axis, relative intensity is not at same scale.

Figure 5.20: Experimental mass spectrum determined for peak number 4 assigned to pentadecane
Now the peak at retention time 17.2 min is analyzed. Table 5.9 shows the formula and molecular weight for peak number 5.

### Table 5.9: Compound assignment of peak number 5

<table>
<thead>
<tr>
<th>Item</th>
<th>Hexadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>$C_{16}H_{34}$</td>
</tr>
<tr>
<td>Formula</td>
<td>$C_{16}H_{34}$</td>
</tr>
<tr>
<td>MW</td>
<td>226.44</td>
</tr>
</tbody>
</table>

In Figure 5.22 the experimentally determined hexadecane mass spectrum and in Figure 5.23 the NIST database, each spectrum has the biggest mass fragmentation at 40, 60, 70, 85, 100, 113, 127, 140, 155, 169, 183 and 197 the final mass peak is at 226 m, corresponding to $C_3H_7$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$ and final $C_2H_5$ fragmentation. Note that y axis, relative intensity is not at same scale.
Figure 5.22: Experimental mass spectrum determined for peak number 5 assigned to hexadecane

Figure 5.23: NIST database hexadecane mass spectrum

Now the peak at retention time 19.5 min is analyzed. Table 5.10 shows the formula and molecular weight for peak number 6.
Table 5.10: Compound assignment of peak number 6

<table>
<thead>
<tr>
<th>Item</th>
<th>Assigned Compound</th>
<th>Heptadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{17}H_{36}$</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>240.47</td>
<td></td>
</tr>
</tbody>
</table>

In Figure 5.24 the determined heptadecane mass spectrum and in Figure 5.25 the NIST database, each spectrum has the biggest mass fragmentation at 40, 60, 70, 85, 100, 113, 127, 140, 155, 169, 183, 197 and 211 the final mass peak is at 240 m, corresponding to $C_3H_7$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$ and final $C_2H_5$ fragmentation. Note that y axis, relative intensity is not at same scale.

Figure 5.24: Experimental mass spectrum determined for peak number 6 assigned to heptadecane
Now the peak at retention time 21.8 min is analyzed. Table 5.11 shows the formula and molecular weight for peak number 7.

**Table 5.11: Compound assignment of peak number 7**

<table>
<thead>
<tr>
<th>Item</th>
<th>Octadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>$C_{18}H_{38}$</td>
</tr>
<tr>
<td>Formula</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>254.49</td>
</tr>
</tbody>
</table>

In Figure 5.26 the determined octadecane mass spectrum and in Figure 5.26 the NIST database, each spectrum has the biggest mass fragmentation at 40, 60, 70, 85, 100, 113, 127, 140, 155, 169, 183, 197, 211 and 225 the final mass peak is at 254 m, corresponding to $C_{3}H_{7}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$, $CH_{2}$ and final $C_{2}H_{5}$ fragmentation. Note that y axis, relative intensity is not at same scale.
Conclusions

Figure 5.26: Experimental mass spectrum determined for peak number 7 assigned to octadecane

Figure 5.27: NIST database octadecane mass spectrum

Now the peak at retention time 23.9 min is analyzed. Table 5.12 shows the formula and molecular weight for peak number 8.
**Table 5.12: Compound assignment of peak number 8**

<table>
<thead>
<tr>
<th>Item</th>
<th>Assigned Compound</th>
<th>Nonadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{19}H_{40}$</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>268.52</td>
<td></td>
</tr>
</tbody>
</table>

In Figure 5.28 the determined nonadecane mass spectrum and in Figure 5.29 the NIST database, each spectrum has the biggest mass fragmentation at 40, 60, 70, 85, 100, 113, 127, 140, 155, 169, 183, 197, 211, 225 and 240 the final mass peak is at 268 m, corresponding to $C_3H_7$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$ and final $C_2H_5$ fragmentation. Note that y axis, relative intensity is not at same scale.

**Figure 5.28: Experimental mass spectrum determined for peak number 8 assigned to nonadecane**
Now the peak at retention time 25.3 min is analyzed based in decanoic acid fragmentation showed in Figure 5.30 from reference [61]. Table 5.13 shows the formula and molecular weight for peak number 8.
Table 5.13: Compound assignment of peak number 8

<table>
<thead>
<tr>
<th>Item</th>
<th>Hexadecanoic acid (palmitic acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>Hexadecanoic acid (palmitic acid)</td>
</tr>
<tr>
<td>Formula</td>
<td>$C_{16}H_{32}O_{2}$</td>
</tr>
<tr>
<td>MW</td>
<td>256.42</td>
</tr>
</tbody>
</table>

In Figure 5.31 the determined palmitic acid mass spectrum and in Figure 5.32 the NIST database, each spectrum has the biggest mass fragmentation at 45, 60, 73, 87, 98, 115, 129, 143, 157, 171, 185, 199, 213, and 227 the final mass peak is at 256 m, corresponding to $COOH$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$ and final $C_2H_5$ fragmentation. Note that y axis, relative intensity is not at same scale.

Figure 5.31: Experimental mass spectrum determined for peak number 8 assigned to palmitic acid
Now the peak at retention time 28.7 min is analyzed. Table 5.14 shows the formula and molecular weight for peak number 9.

Table 5.14: Compound assignment of peak number 8

<table>
<thead>
<tr>
<th>Item</th>
<th>Assigned Compound</th>
<th>Formula</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>Oleic acid</td>
<td>$C_{18}H_{34}O_2$</td>
<td>282.46</td>
</tr>
<tr>
<td>Formula</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td></td>
<td></td>
<td>282.46</td>
</tr>
</tbody>
</table>

In Figure 5.33 the determined oleic acid mass spectrum and in Figure 5.34 the NIST database, each spectrum has the biggest mass fragmentation at 45, 58, 72, 86, 100, 127 and 264 the final mass peak is at 282 m dot not appear but the NIST shows that peak has a lower intensity, corresponding to $COOH$, $CH_2$, $CH_2$, $CH_2$, $CH$, $C_2H_3$, $C_3H_6$ and final $CH_3$ fragmentation. Note that y axis, relative intensity is not at same scale.
Figure 5.33: Experimental mass spectrum determined for peak number 8 assigned to oleic acid

Figure 5.34: NIST database oleic acid mass spectrum

Now the peak at retention time 29 min is analyzed. Table 5.15 shows the formula and molecular weight for peak number 10.
Table 5.15: Compound assignment of peak number 10

<table>
<thead>
<tr>
<th>Item</th>
<th>Stearic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned Compound</td>
<td>C_{18}H_{36}O_{2}</td>
</tr>
<tr>
<td>MW</td>
<td>284.48</td>
</tr>
</tbody>
</table>

In Figure 5.35 the determined stearic acid mass spectrum and in Figure 5.36 the NIST database, each spectrum has the biggest mass fragmentation at 45, 60, 73, 87, 98, 114, 129, 143, 157, 171, 185, 199, 213, 227, 241, and and 255 the final mass peak is at 284 m, corresponding to COOH, CH₂, CH₂, CH₂, CH₂, CH₂, CH₂, CH₂, CH₂, CH₂, CH₂, CH₂ and final C₂H₅ fragmentation. Note that y axis, relative intensity is not at same scale.

Figure 5.35: Experimental mass spectrum determined for peak number 10 assigned to stearic acid
Now the peak at retention time 47 min is analyzed and assigned. Table 5.16 shows the formula and molecular weight for peak number 11.

<table>
<thead>
<tr>
<th>Item</th>
<th>Assigned Compound</th>
<th>Monoglyceride R16 (Isopropyl palmitate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{19}H_{38}O_2$</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>298.50</td>
<td></td>
</tr>
</tbody>
</table>

In Figure 5.37 the determined monoglyceride R16 (Isopropyl palmitate) mass spectrum and in Figure 5.38 the NIST database, each spectrum has the biggest mass fragmentation at 43, 60, 98, 102, 129, 143, 157, 171, 185, 199, 213, 227, 239, and 257, corresponding to $C_3H_7$ (isopropyl), $O$, $OC_2H_4$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, and the final mass fragmentation is at $m/z=298$ corresponding to $C_{15}H_{31}COOC \cdot (CH_3)_2$. Note that y axis, relative intensity is not at same scale.
Figure 5.37: Experimental mass spectrum determined for peak number 11 assigned to monoglyceride R16

Figures 5.38: NIST database monoglyceride R16 mass spectrum

Now the peak at retention time 50 min is analyzed and assigned. Table 5.17 shows the formula and molecular weight for peak number 12.
Table 5.17: Compound assignment of peak number 12

<table>
<thead>
<tr>
<th>Item</th>
<th>Assigned Compound Monoglyceride R18 (Isopropyl stearate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{21}H_{42}O_2$</td>
</tr>
<tr>
<td>MW</td>
<td>326.55</td>
</tr>
</tbody>
</table>

In Figure 29 the determined palmitic acid mass spectrum and in Figure 30 the NIST database, each spectrum has the biggest mass fragmentations at 43, 60, 98, 102, 129, 143, 157, 171, 185, 199, 213, 227, 239, and 256 the final mass peak is at 298 m, correspondig to $C_3H_7$ (isopropryl), $O$, $OC_2H_4$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, $CH_2$, and the final mass fragmentation is at $m/z=325$ corresponding to $C_{17}H_{35}COOC \ast (CH_3)_2$. Note that y axis, relative intensity is not at same scale.

Figure 5.39: Experimental mass spectrum determined for peak number 11 assigned to monoglyceride R18
Now the Figures 5.41 to 5.47 shows the chromatograms with peak assignment for each reaction in batch operation.

**Figure 5.40:** NIST database monoglyceride R18 mass spectrum

**Figure 5.41:** Reaction 1 R1 chromatogram of liquid sample resulted of MS-GC analysis for batch operation
**Figure 5.42:** Reaction 2 R2 chromatogram of liquid sample resulted of MS-GC analysis for batch operation

**Figure 5.43:** Reaction 3 R3 chromatogram of liquid sample resulted of MS-GC analysis for batch operation
**Figure 5.44:** Reaction 4 R4 chromatogram of liquid sample resulted of MS-GC analysis for batch operation

**Figure 5.45:** Reaction 5 R5 chromatogram of liquid sample resulted of MS-GC analysis for batch operation
**Figure 5.46:** Reaction 6 R6 chromatogram of liquid sample resulted of MS-GC analysis for batch operation

**Figure 5.47:** Reaction 7 R7 chromatogram of liquid sample resulted of MS-GC analysis for batch operation
Appendix B: Operating procedure for the high pressure TBR

This standard operating procedure (SOP) describes the normal operation of a hydrotreating reactor palm oil based on reference [62]. After packing and sealing the reactor as shown in Figure 4.2 follow the steps below:

1. Close the valve of gas liquid separator
2. Regulating the output pressure nitrogen cylinder to cylinder 1 bar
3. Start the flow of nitrogen and select a flow of 25 SCCM
4. Start the furnace and select the operating temperature
5. After reaching the operating temperature regulating outlet pressure nitrogen cylinder to the operating pressure
6. Start the liquid pump and select the volumetric flow according to previously established residence time
7. Stop the nitrogen flow, adjust the output pressure of the hydrogen cylinder to the operating pressure, and start the flow of hydrogen
8. Select the hydrogen flow according to the flow of liquid. The flow of hydrogen is 20 times the molar flow of oil
9. Wait until the steady state (more than six times the residence time of the liquid)
10. Drain the gas-liquid separator
11. After reaching twelve times the reactor residence time take gaseous (500 mL) and liquid (2 mL) samples into sample bags and vials respectively. Be careful when taking gas samples. Learn the proper use of the sampling bags.

To shut down the reactor follow the steps below:

1. Depressurize the reactor to atmospheric pressure, then stop the flow of hydrogen. Regulate the output pressure of the nitrogen cylinder to atmospheric pressure, and start the flow of nitrogen

2. Drain liquid phase

3. Select at room temperature set-point, wait for the system to cool completely and turn off the furnace.

4. Stop the nitrogen flow.

5. Remove and drain the reactor bed.
Appendix C: Temperature profiles inside the reactor without chemical reaction

The temperature inside the reactor was measurement using a 1/16 inches thermocouple. The furnace temperature was controlled with a external reactor thermocouple. The temperature in the reactor was measurement placed 2 cm through the reactor, also a nitrogen flow 50 SCCM at room temperature was feed. Figures 5.48, 5.49, 5.50 shows the temperature profiles inside the reactor at 337, 355 and 370°C as set-point temperature of the reactor. The isothermal range inside the reactor was close to 5 cm, therefore a catalyst bed was put in this zone.

![Temperature profile graph](image)

**Figure** 5.48: Temperature profile at 337°C as temperature outside the reactor
Figure 5.49: Temperature profile at 355°C as temperature outside the reactor

Figure 5.50: Temperature profile at 370°C as temperature outside the reactor
Appendix D: Chomatograms results of the liquid samples characterization for continuous set up

Now the Figures 5.51 to 5.57 shows the chromatograms with peak assignment for each reaction in continuous operation.

**Figure 5.51**: Reaction 1 R1 chromatogram of liquid sample resulted of MS-GC analysis for continuous operation
Figure 5.52: Reaction 2 R2 chromatogram of liquid sample resulted of MS-GC analysis for continuous operation
Figure 5.53: Reaction 3 R3 chromatogram of liquid sample resulted of MS-GC analysis for continuous operation
Figure 5.54: Reaction 4 R4 chromatogram of liquid sample resulted of MS-GC analysis for continuous operation
**Figure 5.55**: Reaction 5 R5 chromatogram of liquid sample resulted of MS-GC analysis for continuous operation

**Figure 5.56**: Reaction 6 R6 chromatogram of liquid sample resulted of MS-GC analysis for continuous operation
Figure 5.57: Reaction 7 R7 chromatogram of liquid sample resulted of MS-GC analysis for continuous operation
References


REFERENCES


