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ONE-POT HYDROLYSIS-HYDROGENATION OF REFINED PALM OIL USING FORMIC ACID AS CATALYST AND HYDROGEN DONOR IN PRESENCE OF Ni/SiO_2 CATALYST

Rio de Janeiro – RJ/Brazil
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Master's dissertation presented to the Graduate Program in Chemical and Biochemical Processes Engineering, School of Chemistry, Federal University of Rio de Janeiro, as partial requirement for obtaining the Masters of Science Degree in Chemical and Biochemical Processes Engineering

Advisors:
PhD. Donato Alexandre Gomes Aranda
PhD. João Monnerat Araujo Ribeiro de Almeida

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DEDICATION

All the achievements of this period of my career I owe to the most important person in my life, my wonderful boyfriend Mateus. I dedicate this milestone to him, because his unconditional support, patience, encouragement and, above all, love, helped me to come this far. I know it have been some rough years for me, distant from everything I know, but the constant growing with him made it all worth it.

I also dedicate this work in the memory of one of the wisest and humble person I have ever known, my mentor Dr. Sam Mannan. Because his support encouraged me to be where I am today, I could never thank him enough for inspiring me to follow my dreams and having always the right words to say when I needed it. I will cherish forever his memory, and will never forget all of the teachings and opportunities to grow that I had with him.

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Whatever you do, do your best

— Sam Mannan

“The meeting of two personalities is like the contact of two chemical substances: if there is any reaction, both are transformed.”

— Carl Gustav Jung

“It is never wise to seek or wish for another’s misfortune. If malice or envy were tangible and had a shape, it would be the shape of a boomerang.”

— Charley Reese

ABSTRACT

ANGARITA, Laura Viviana. **One-pot hydrolysis-hydrogenation of refined palm oil using formic acid as catalyst and hydrogen donor in presence of nickel catalyst**. Rio de Janeiro, 2019. Dissertation (Master's in Chemical and Biochemical Processes Engineering) - School of Chemistry, Federal University of Rio de Janeiro, Rio de Janeiro, 2019.

This study proposes a new process to produce a saturated fatty acids blend from palm oil, in a one-pot hydrolysis-hydrogenation reaction using a hydrogen donor. Without the use of molecular hydrogen, formic acid is employed as internal hydrogen donor while, at the same time, it acts as homogenous catalyst in the hydrolysis reaction. The catalytic transfer hydrogenation is carried out by a nickel catalyst. The production of saturated fatty acids, especially stearic acid (a blend of approximately equal amounts of stearic and palmitic acids and small amounts of oleic acid), is important for different markets such as personal care, food, pharmaceutical, and industry, due the versatility of the product. The reactions were carried out in a Parr reactor with a capacity of 100 mL, at 190°C, 20 bar of nitrogen pressure, and 3 wt% of heterogeneous catalyst. Initial screening tests performed using crude palm oil and soy oil, with Ni/Al_2O_3 and commercial Raney nickel catalyst, but the result was unsatisfactory due to nickel saponification of the catalyst. Subsequently, a new set of tests were performed with refined palm oil and Ni/SiO_2 catalyst (resistant to nickel soap formation) to overcome the drawbacks. All catalysts were characterized to understand their performance in the reaction. On the other hand, to monitor the extent of hydrolysis and hydrogenation the products were analyzed with the acid value and iodine value methods. For the identification of the sample composition infrared spectroscopy, thin-layer and high-performance liquid chromatography were employed. It was found that the best hydrolysis conversion (129 mg NaOH/g) was obtained with the highest level of formic acid concentration (25:1 molar ratio of formic acid/oil). Nonetheless, despite the amount of formic acid and the reaction time, the iodine value got stagnated at approximately 19 $gI_2/100g$ with an extent of hydrogenation of 64%. The GC-FID results showed selectivity towards hydrogenation of polyunsaturated fatty acid chains with low conversion of oleic acid, indicating partial hydrogenation. Formic acid was found suitable as hydrogen donor and homogenous catalyst, however, complete hydrogenation was not achieved.

Keywords: Hydrolysis; hydrogenation; hydrogen donor; palm oil, saturated fatty acids.

RESUMO

ANGARITA, Laura Viviana. **One-pot hydrolysis-hydrogenation of refined palm oil using formic acid as catalyst and hydrogen donor in presence of nickel catalyst**. Rio de Janeiro, 2019. Dissertation (Master's in Chemical and Biochemical Processes Engineering) - School of Chemistry, Federal University of Rio de Janeiro, Rio de Janeiro, 2019.

Este estudo propõe um novo processo para a produção de uma mistura de ácidos graxos saturados a partir de óleo de palma, em uma reação simultanea de hidrólise e hidrogenação usando um doador de hidrogênio. Sem o uso de hidrogênio molecular, o ácido fórmico é empregado como doador interno de hidrogênio e, ao mesmo tempo, atua como catalisador homogêneo na reação de hidrólise. A hidrogenação catalítica por transferência é realizada por um catalisador de níquel. A produção de ácidos graxos saturados, especialmente o ácido esteárico é realmente importantede grande relevância para diferentes mercados como cosméticos, alimentos, farmacêutico e industrial, devido à versatilidade do produto. As reações foram realizadas em um reator Parr com capacidade de 100 mL, a 190 ° C, 20 bar de pressão de nitrogênio e 3 %p de catalisador heterogêneo. Testes de triagem foram realizados usando óleo de palma bruto e óleo de soja, com catalisadores Ni/Al_2O_3 e niquel raney, mas o resultado foi insatisfatório devido à saponificação de níquel do catalisador. Posteriormente, um novo conjunto de testes foi realizado com óleo de palma refinado e catalisador de Ni/SiO_2 (resistente à formação de sabão de níquel) para superar os problemas encontrados. Todos os catalisadores foram caracterizados para entender seu desempenho na reação. Por outro lado, para monitorar a extensão da hidrólise e hidrogenação, os produtos foram analisados com os métodos de índice de acidez e índice de iodo. Para a identificação da composição da amostra utilizou-se espectroscopia com infravermelho, cromatografia líquida de alta eficiência e camada fina. Verificou-se que a melhor conversão de hidrólise ocorreu com o nível mais elevado de concentração de ácido fórmico. No entanto, apesar da quantidade de ácido fórmico e do tempo de reação, o valor do iodo ficou estagnado em aproximadamente 19 $gI_2/100g$, com uma extensão de hidrogenação de 64%. Os resultados de GC-FID mostraram seletividade para hidrogenação de cadeias de ácidos graxos poliinsaturados com baixa conversão de ácido oleico, indicando hidrogenação parcial. O ácido fórmico foi considerado adequado como doador de hidrogênio e catalisador homogêneo, entretanto, hidrogenação completa não foi alcançada.

Palavras-chave: Hidrólise; hidrogenação; doador de hidrogênio; óleo de palma, ácidos graxos saturados.

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ABBREVIATIONS LIST

AV	Acid value
BET	Brunauer-Emmett-Teller
CTH	catalytic transfer hydrogenation
DTG	differential thermogravimetry
FA	Formic acid
FAME	Fatty acid methyl ester
FFA	free fatty acids
GC-FIC	Gas Chromatography with Flame-Ionization Detection
IR	infrared spectroscopy
IV	Iodine value
IWI	incipient wetness impregnation
NiAl	Nickel alumina
NiSi	Nickel Silica
POFA	palm oil fatty acid
RN	Raney Nickel
RPM	revolutions per minute
RPO	refined palm oil
STP	standard conditions of temperature and pressure
TG	triglycerides
TGA	Thermogravimetric analysis
TLC	Thin-layer Chromatography
TPR	Temperature-programmed reduction
UFRJ	Universidade Federal de Rio de Janeiro
w/o	Without
XRD	X-ray diffraction

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1 INTRODUCTION

Palm oil is an important commodity worldwide because of its wide applicability in different markets (BASIRON, 2015; MBA *et al.*, 2015). In Brazil, *Palmeira de Dendê*, how it is called, is the third most produced plant in the country (ABRAPALMA, 2011). The main components of an oil are the triglycerides, and its physical properties depends on the structure and distribution of the fatty acids present. Palm oil consists mainly of triglycerides with a C_{16}-C_{18} chain length of unsaturated and saturated fatty acids. In the oleochemistry industry exists a growing demand for hydrogenated fatty acids (BIERMANN *et al.*, 2011; ZIELIŃSKA & NOWAK, 2014) since its application can range from food to non-food purposes (CHARAM, 2013). Saturated fatty acids are usually obtained through the combination of two processes, hydrolysis and hydrogenation.

To obtain highly hydrogenated fatty acids it is necessary a large amount of hydrogen to favor the reaction (CHENG *et al.*, 2013). Such requirement presents some technical and logistical challenges, especially in remote places where the access to the gas is precarious or inexistent, making the process not profitable or less attractive. Additionally, industry nowadays is more concerned about replacing feedstocks from fossil origin for renewable ones, as is the case of hydrogen.

A suitable alternative, studied along the years, is the substitution of molecular hydrogen for hydrogen donors in a process called catalytic transfer hydrogenation (CTH). CTH is a safe, simple and eco-friendly method. The compounds used as hydrogen donors are easy to store, handle, and transport, unlike pure hydrogen gas under pressure. Some commonly used hydrogen donors are cyclohexene, glycerol, ethanol, isopropanol, limonene, sodium and ammonium formate, and formic acid (KOBE *et al.*, 1991; MARTINELLI *et al.*, 2005; WOLFSON & DLUGY, 2009; ROSANA DE SOUZA SCHNEIDER *et al.*, 2010; HWANG *et al.*, 2016).

The present work studied the use of formic acid as the hydrogen donor. Formic acid is a perfect candidate to be the hydrogen donor agent due to its low toxicity, cost, and high stability (LIU et al., 2015). Furthermore, formic acid is considered a renewable reagent and can be obtained in large quantities via hydrogenation of waste carbon dioxide from industry, biomass processing and artificial photosynthesis, which makes it easily available and affordable (LEITNER, 1995; JIN *et al.*, 2008; GONG *et al.*, 2014; LIU *et al.*, 2015). Additionally, formic acid can be employed as homogenous catalyst in the hydrolysis reaction of oil at the same time.

Simultaneous hydrolysis and hydrogenation is a relatively new process, and information about it is scarce. However, the unification of the two processes present great advantages over the conventional one, where two steps are required to obtain the desired product. The objective of this work is the production of saturated fatty acids from palm oil, using formic acid as hydrogen donor in a one-pot hydrolysis-hydrogenation reaction. Commercial nickel based catalyst was used to carry out the CTH reaction and formic acid, besides working as a hydrogen donor, is simultaneously employed as homogenous catalyst in the hydrolysis of the oil.

2 SCOPE

2.1 GENERAL SCOPE

Obtain a blend of saturated fatty acids, from palm oil, using formic acid as homogenous catalyst and hydrogen donor in a one-pot hydrolysis-hydrogenation reaction.

2.2 ESPECIFIC SCOPES

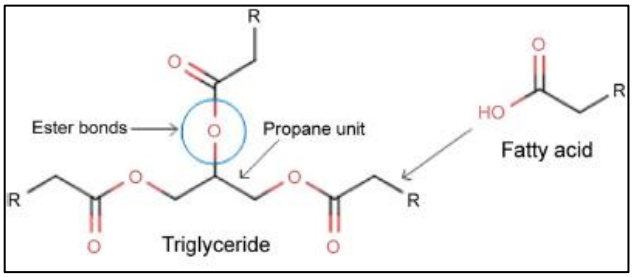
- Evaluate the performance of formic acid in the hydrolysis reaction, and in the hydrogenation reaction as internal hydrogen donor.
- Evaluate the efficiency of Ni/Al_2O_3, Raney Nickel and Ni/SiO_2 catalyst in the conversion of unsaturated fatty acids into saturated fatty acids.
- Catalyst characterization through thermogravimetric, textural and X-ray diffraction analysis.
- Product characterization through acid value, iodine value, infrared spectroscopy, thin-layer chromatography and gas chromatography with flame-ionization detection.
- Validate the viability of achieving hydrolysis and hydrogenation in a one-pot reaction.

3 REVIEW

3.1 TRIGLYCERIDES

Triglycerides can be found in oils and fats from vegetable and animal origin, and residual tallow. They are esters of glycerin and fatty acids as shown in Figure 1 (ROGERS & ZHENG, 2016). The properties of different oil/fats depends directly of the length of the fatty acid chain and the presence of saturated or unsaturated bonds. Some triglycerides can be used for edible purposes, others cannot. The length of the chain in fatty acids run from C_4-C_{24} mostly.

Figure 1. Structure of triglycerides and fatty acids

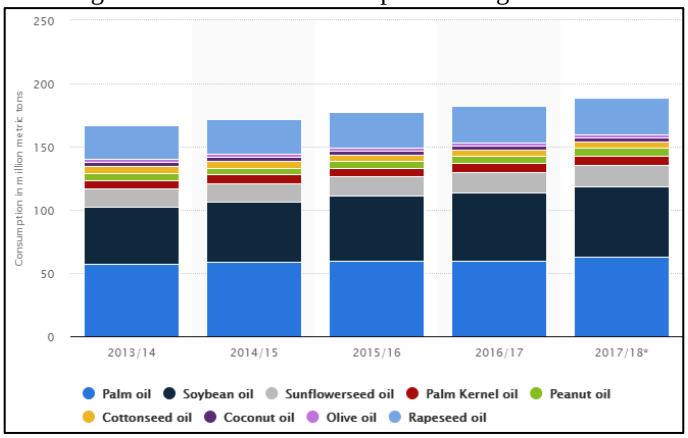


(NEUZA, 2009)

The most important vegetable oils worldwide are soybean oil and palm oil. The consumption forecast for 2018 was 62.92 MMT (million metric tons) for palm oil and 55.99 MMT for soybean oil, Figure 2.

In virtue of its importance and global availably, palm oil is the focus of this research. An overview and a description of its properties will be presented below.

Figure 2. Worldwide consumption of vegetable oils



(STATISTA, 2018)

3.1.1 Palm oil

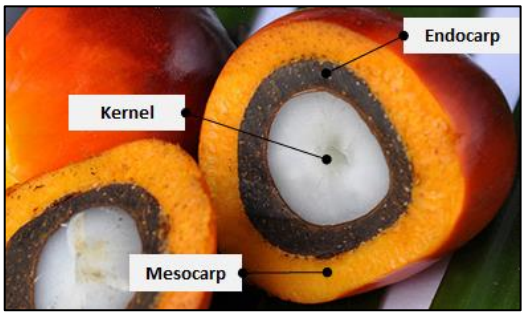
The use and application of palm oil in different industries has been expanded worldwide during the past years. Since 2012, palm oil was responsible for 30% of the fats and oils global production, overcoming soybean oil as the most important oil in the world (MBA *et al.*, 2015).

Palm oil is extracted from the palm tree *Elais guineenses*, an ancient tropical plant native from West African countries. The biggest palm crops, responsible for 86% of the global production are located in Malaysia and Indonesia. The remaining crops are found in tropical regions such as Nigeria, Thailand, Colombia, Papa Guinea, Cote d'Ivoire, India and Brazil (MANCINI *et al.*, 2015).

The Portuguese introduced the plant in Brazil and other tropical countries in the fifteenth century. *Palmeira de Dendê*, how it is called in Brazil, is the third most produced plant in the country, just behind soy and cotton, with an annual production yield around 370 thousand tons, accounting for 0,57% of the worldwide production (ABRAPALMA, 2011). In Brazil, the biggest crops are located in Pará, Amazonas, Amapá and Bahia, being Pará the biggest palm oil producer with 80% of the national production.

The palm's fruit produces two types of oil as showed in Figure 3: palm oil that comes from the external part of the fruit, known as mesocarp, and the palm kernel oil extracted from the seed. Both oils are considered as one of the most versatile raw materials since they can be used for food and non-food purposes. Some of the industries accounted for its use are consumer retail food and snacks, personal care and cosmetics, biofuel and energy, animal feed, pharmaceutical, industrial and food services (SAMBANTHAMURTHI *et al.*, 2000; GREENPALM, 2018).

Figure 3. Palm fruit



(INDOENERGY, 2014)

Crude palm oil can contain different compounds such as triglycerides (TGs), vitamin E, carotenoids, phytosterols, as well as impurities such as phospholipids, free fatty acids (FFAs), gums, and lipid oxidation. Its distinctive red color is caused by the high quantity of beta-carotene content. It is important to state that triglycerides in the palm oil defines most of its physical characteristics such as melting point and crystallization behavior (MANCINI *et al.*, 2015). As a result of its chemical composition, palm oil has the best oxidative stability when compared with other vegetable oils (SAMBANTHAMURTHI *et al.*, 2000).

Palm oil has a saturated to unsaturated fatty acids composition ratio of approximately 1:1, which influences on its semi-solid aspect at room temperature. Even though the composition of the oil might differ slightly from crop to crop thanks to geographical influences, 50% of the saturated fats corresponds mainly to palmitic and stearic acid, and the remaining 50% to unsaturated fats oleic and linoleic acids (MANCINI *et al.*, 2015).

Table 1, shows the composition range of fatty acids presents in the palm oil (FIRESTONE, 2013). Some physicochemical properties of palm oil, collected from different references, are presented in Table 2.

Table 1. Fatty acid composition in palm oil

Fatty Acid Trivial name	**Fatty Acid Systematic name**	**Shorthand (chain length: double bonds)**	**Palm oil (%)**
Lauric acid	Dodecanoic acid	(12:0)	≤ 0,4
Myristic acid	Tetradecanoic acid	(14:0)	0,5 – 2,0
Palmitic acid	Hexadecanoic acid	(16:0)	40,0 – 48,0
Palmitoleic	cis-9-Hexadecenoic acid	(16:1)	≤ 0,6
Stearic acid	Octadecanoic acid	(18:0)	3,6 – 6,5
Oleic acid (Ω 9)	cis-9-Octadecenoic acid	(18:1)	36,0 -44,0
Linoleic acid (Ω 6)	9,12-Octadecadienoic acid	(18:2)	6,5 – 12,0
Linolenic acid (Ω 3)	9,12,15-Octadecatrienoic acid	(18:3)	≤ 0,5
Arachidic acid	Eicosanoic acid	(20:0)	≤ 1,0
Gadoleic acid	cis-9-Eicosenoic acid	(20:1)	≤ 1,2
Behenic acid	Docosanoic acid	(22:0)	≤ 0,1
Lignoceric acid	Tetracosanoic acid	(24:0)	≤ 1,2

Table 2. Physicochemical properties of palm oil

Property	**Value**	**Reference**
Flash point °C	314	(SHAHIDI, 2005)
Iodine value g/100g	51-54	(KARLESKIND, 1992)
	49-55	(FIRESTONE, 2013)
Melting point °C	30,8 – 37,6	(ANNEKEN *et al.*, 2012)
	27,0- 45,0	(KARLESKIND, 1992)
	33-40	(FIRESTONE, 2013)
Density g/ml	0,9210-0,9350 (15 °C)	(ANNEKEN *et al.*, 2012)
	0,8981(40 °C)	(UNIPALMA))
	0,891 (50 °C) – 0,899 (20 °C)	(FIRESTONE, 2013)
Saponification value	195-205	(KARLESKIND, 1992)
mgKOH/g oil	190-209	(FIRESTONE, 2013)
Acidity (%Oleic acid)	<0,3	(FIRESTONE, 2013)

As stated in this section, palm oil is an important commodity worldwide due to its wide applicability in different markets (MBA *et al.*, 2015). The vast production of the oil makes the accessibility to the raw material easy and affordable. Nonetheless, the biggest demand in the oleochemistry industry is for hydrogenated fatty acids rather than crude oil (BIERMANN *et al.*, 2011; ZIELIŃSKA & NOWAK, 2014; BASIRON, 2015) and saturated fatty acids have more commercial value than palm oil.

3.2 SATURATED FATTY ACIDS

Palm oil hydrogenation produces a saturated C_{16} and C_{18} fatty acids chains' blend, a product with high commercial value, called stearic acid. Commercially, stearic acid is a mixture of approximately equal amounts of stearic and palmitic acids and small amounts of oleic acid. Such mixture is solid at ambient temperature and has a waxy texture.

Hydrogenation of oils and fatty acids is a business in over 60 countries world-wide. The aim of such important industrial reaction is to obtain monounsaturated and saturated fatty acids, to get attractive organoleptic changes and a greater chemical stability, especially in products with high temperature applications, high resistance to oxidation and enhanced shelf life (ANNEKEN *et al.*, 2012).

Because of the high stability and low iodine value, stearic acid has many niche applications. Stearic acid market is segmented in personal care, food, pharmaceutical and biomedical science, and industrial uses. Some of the applications on consumer-related applications are soaps, detergents, personal care products, cosmetics as surfactant and emulsifying agent, and food on the flavoring and fragrance sectors. Examples of industrial applications are in the fabrication of lubricant, plastics and ceramics, auxiliary in rubber vulcanization, manufactures of tires, greases, candles, pharmaceutical, textile, and paint sectors (PINTO & LANÇAS, 2006; AMCDOBRASIL, 2016; EVONIKCATALYST, 2016a).

The application of the stearic acid will depend on different properties. Two main properties are the iodine value and acid value. On Table 3 are some of its application on industry and the technical specification needed.

Table 3. Industry applications of stearic acid and specifications

Applications	Iodine Value (g/100g)	Acid Value (mgKOH/g)
Cosmetics and chemical specialty	1	205-212
Textile auxiliaries, plastics, cosmetics and stearates	3	205-210
Textiles and plastics	3	195-203
Activated calcium carbonate industry, buffing compounds & stearates	3	198-200
Buffing compound, stearates & waterproofing cements	3	196-200
Metal polishes & metallic stearates	9	192-197
Type rubber compounding	9	190-195
General rubber compounding	9	180-195
Greases	15	175-185

(CHARAM, 2013)

Different market research companies (mordorintelligence.com, icis.com, grandviewresearch.com, researchandmarkets.com, marketresearchfuture.com) envision that stearic acid market is expected to growth during the period between 2018 and 2023. Personal care is projected to be the fastest-growing application influencing in the stearic acid market rise.

The market forecast suggests a business opportunity on the demand of stearic acid, caused by the growth of several applications and the great versatility of the product. Commercially stearic acid is sold in form of scams, granulated or power. Table 4presents the average price of the crude palm oil and stearic acid in the market. The information was taken for the January 2019 weekly report from aboissa.com.br.

Table 4. Palm oil and stearic acid market price

Product	Average price
Crude palm oil	538 (US$/ton)
Refined palm oil	533 (US$/ton)
Stearic acid – double pressed	3300 (R$/ton)
Stearci acid – triple pressed	3500 (R$/ton)
Stearic acid -vegetable	900 (US$/ton)

(Aboisa.com.br)

There are two main approaches for industrial production of stearic acid: compression and hydrogenation methods. Compression method consists in the hydrolysis of the raw material in the presence of a catalysis, proceeded by washing and filtration to remove the glycerin and catalyst, distillation to improve color and purity, cooling and freezing. Afterwards, the cake formed is pressed in a large hydraulic press for removal of oleic acid, then the product is remelted, recast and pressed a second time at elevated temperature to remove additional oleic acid (CRANOR, 1929; MYERS & MUCKERHEIDE, 1942). Depending on the application, a triple-pressed process is necessary.

Hydrogenation method consists in the hydrogenation of the fats. Subsequently, the hardened fat is distilled to purify the product and then splitted to produce fatty acids. The saturated fatty acids obtained are the commercial stearic acid (JOEL, 1928).

The present study will focus on obtaining stearic acid by hydrolysis of the oil and hydrogenation. Both processes will be explained in the following section.

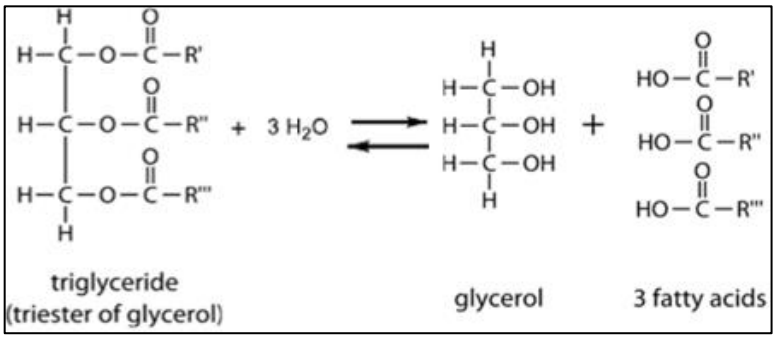
3.3 HYDROLYSIS AND HYDROGENATION OF OILS AND FATS

Hydrolysis is a process where the oil/fats are decomposed into fatty acids and glycerol in an aqueous environment. With the addition of hydrogen, the fatty acids are hydrogenated to saturated fatty acids, which are highly valuable for different industries. Both reactions can occur simultaneously and randomly. In the following sections hydrolysis and hydrogenation reactions will be explained.

3.3.1 HYDROLYSIS OF OILS AND FATS

Palm oil is 95% formed by triglycerides, therefore, the chemistry of palm oil is dominated by the reactions of the ester group (SAMBANTHAMURTHI *et al.*, 2000). The process of hydrolysis is a chemical reaction where water breaks down the bonds of a substance, in this case the triglycerides. The breakage of the ester bonds in the triglyceride molecule produces glycerol and free fatty acids (carboxylic acids) as illustrated in Figure 4.

Figure 4. Hydrolysis of triglyceride.



Hydrolysis can be carried out by enzymes, homogeneous or heterogeneous catalyst, and non-catalytic processes like under subcritical and supercritical conditions (DIAZ, 2012; SANTOS *et al.*, 2015). Non-catalytic reactions require extreme operational conditions or long

reaction times. In the other hand, catalytic reactions can be executed under mild conditions. The catalyst promotes the solubilization of the triglycerides into the water, giving a better contact within the reagents and a selectivity towards the desired product. In hydrolysis process, triglycerides are first converted into diglycerides, and those are hydrolyzed to monoglycerides, then into glycerol and fatty acids. Hydrolysis is a first order, endothermic and reversible reaction (MILLS & MCCLAIN, 1949; LOGAN *et al.*, 1978; BUENO, 2005; MINAMI & SAKA, 2006; SANTOS *et al.*, 2015).

In 1853 Richard Tilghman discovered that, while subjecting fat and water to a high degree of heat at a certain pressure (to prevent the water to vaporize), fatty acids and glycerin can be formed. However, special equipment or procedures for such process were not available at that time (BARNEBEY & BROWN, 1948). A step forward was taken by TWITCHELL (1898). In his patent he describes a process using an open tank, where the fat or oil is placed with the addition of 50% of water and 1% of acid catalyst (sulfofatty acid) to speed up the reaction. Then, the mixture is boiled by open steam process (100 °C and 1 bar) for around 12-20 hours. Despite the novelty of the process at the time, it was highly energy and time consuming and the fat splitting was only 80-85%, producing also a significant amount of acid sludge.

MILLS (1935) and Proctec and Gamble co, presented a patent on continuous countercurrent hydrolysis of fat. The reaction was carried out in a vertical closed vessel at high temperature and sufficient pressure, enough to maintain the water in liquid state. The invention was presented as an improvement of the prior processes for hydrolysis, where the aim was to obtain higher yields and rapid rate of splitting in a continuous operation. ITTNER (1936) in company with Colgate-Palmolive Co, developed the patent for hydrolysis of fats and oils. It is stated that every fat oil has an upper temperature limit, which, beyond that, the solubility of the water in the fatty acid is too high to permit the process to be carried out. Therefore, it was found that in temperatures above 200 °C at a pressure of 14 bar during 3 hours, the autocatalytic reaction is satisfactory. For his study, the process was performed in a semi-continuous reactor, where the fatty material and the water are in countercurrent flow. The amount of water use is 8,3 wt% of triglyceride for coconut oil and 6,4 wt% for tallow. Under these conditions, the conversion to fatty acids was approximately 92 %.

MILLS & MCCLAIN (1949) then presented a study for the hydrolysis reaction in a batch autoclave without catalyst. They concluded that the amount of water dissolved in the oil phase varies with temperature. It was also found that at about 321 °C, every proportion of tallow and water formed a single phase, and 293 °C was needed for coconut oil to achieve the same

solubility. The maximum amount of splitting that can occur is determined by the glycerol concentration in the aqueous phase.

The best known countercurrent industrial process is the Colgate-Emery process. In this process fat/oil and water (40-50 wt% of fat) reacts in a column in the absence of catalyst, at temperatures of 250-330 °C and pressure of 50-60 bar for around 2-3 hours. The conversion is high, over 95 % (BARNEBEY & BROWN, 1948). However, it has an intensive energy consumption, requires special and expensive equipment, and is not well suited for low-cost oil. Commercially, batch autoclaving to hydrolyze vegetable is performed at 100-250 °C under autogenous pressure of about 20-45 bar, where the non-catalytic reaction can be carried out in a shorter time (LOGAN *et al.*, 1978; POURZOLFAGHAR *et al.*, 2016; FORERO-HERNANDEZ *et al.*, 2017).

3.3.1.1 Sub and supercritical hydrolysis

Sub and supercritical fluids such as water and carbon dioxide are employed on autocatalytic reactions. The use of these fluids avoids the need of catalyst consumption, which represents a huge economic and environmental advantage. However, the major drawbacks of the high temperature process as stated above are: It is costly, energy intensive, for the high temperatures and pressure necessary to reach such conditions and to cool down the reactor when the reaction is completed and it requires the use of large reactors made of expensive corrosive-resistant material (ANNEKEN *et al.*, 2012; SANTOS *et al.*, 2015). Nonetheless, under those special conditions, water is capable of dissolving a wide variety of organic solutes and increase its solubility in hydrophobic substance such as oils and fats (KOCSISOVÁ *et al.*, 2006). This phenomenon occurs because as temperature increases, the dielectric constant of the water decreases, increasing the solubility of the oil in the aqueous phase (HOLLIDAY *et al.*, 1997; KING *et al.*, 1999; MILLIREN *et al.*, 2013). At subcritical temperatures, water displays dielectric properties similar to methanol, ethanol and acetone. In conclusion, at high temperatures, water acts like solvent, reactant and catalyst for the hydrolysis reaction (JU *et al.*, 2013). Under subcritical conditions, water is at 100-373 °C and a pressure is up to 50 bar. Under supercritical conditions, water temperatures are over 374 °C a pressures are up to 218 bar (HOLLIDAY *et al.*, 1997; SAKA, 2006).

A comparative study performed to correlate hydrolysis of three different oils by subcritical water and supercritical water is presented by HOLLIDAY *et al.* (1997). In this research, the temperatures used to study the influence on hydrolysis of triglycerides (TG) were

250-375 °C. The feedstocks studied were soybean oil, linseed oil, and coconut oil in a batch reactor vessel with 35,5 mL of volume. The volumetric ratio was 6,25:1 water/oil. The results showed that hydrolysis for subcritical water occurs rapidly within 15-20 min, yielding 97 % or better conversion. Linseed oil took the longest to hydrolyze. On the other hand, supercritical water tended to degrade thermally the reactants and products under the studied conditions.

KOCSISOVÁ *et al.* (2006) studied the hydrolysis of refined edible rapeseed oil in a continuous tubular reactor at 280-340 °C; and confirmed that hydrolysis of TG obeys the first-order kinetic equation and within subcritical hydrolysis a partial change in the *cis*-to-*trans* configuration and partial dimerization of the unsaturated FFA take place. In the experiment were observed conversions higher than 95 % at a temperature of 340 °C within a reaction time of 12 min for a 1:2 (v) oil/water ratio.

Meanwhile, some hypothesis about how free fatty acids (FFA) act like an acid catalyst have been studied for authors like MINAMI & SAKA (2006); ALENEZI *et al.* (2009); MILLIREN *et al.* (2013). ALENEZI *et al.* (2009) studied the non-catalytic hydrolysis of sunflower under subcritical water. The experiments were conducted in a tubular reactor with a temperature range of 270-350 °C at 200 bar. The water/oil ratio was 50/50 v/v, obtaining a 93,5% of conversion in 15 min of reaction with the higher temperature. MILLIREN *et al.* (2013) studied a kinetic model for the hydrolysis of soybean oil in subcritical water in the temperature range of 250-300 °C. During some runs, FFA was added to the charge to validate the autocatalytic nature of the reaction. Such theory was confirmed for all three authors mentioned. The addition or existence of FFA increases the rate of hydrolysis, suggesting that its presence on the oil act as an acid catalyst, giving way to an autocatalytic reaction.

3.3.1.2 Hydroesterification

Hydrolysis is also used in the production of biodiesel. Such process is called hydroesterification process and consists in a two-step reaction. The first step is the vegetable oil hydrolysis and production of fatty acids. The second step takes the fatty acids and pass them through a chemical process called esterification using an alcohol (methanol or ethanol) (SANTOS *et al.*, 2015). This process allows to use low quality raw material with high acidity index and humidity. Conventional biodiesel production takes places through transesterification process, where alkaline catalyst is normally used. This process presents some disadvantages like the purification steps to remove the catalyst from the product and the saponified products from FFA, energy intensity, high production costs and the limitation of using low-cost

feedstocks. Consequently, hydroesterification process is presented as a catalyst-free process alternative that overcome such drawbacks (POURZOLFAGHAR *et al.*, 2016).

MINAMI & SAKA (2006) designed a process for biodiesel production using hydroesterification in a two-step method. This experiment was performed in a flow-type reactor using rapeseed oil as feedstock, water and methanol as solvents. The two-step method presents first the hydrolysis of the oil/fat using subcritical water, and second, a subsequent methyl esterification of the fatty acid to fatty acid methyl ester (FAME) under supercritical methanol. The hydrolysis is performed at 200 bar with a 1:1 volume ratio of water/triglyceride. Under a temperature of 290 °C was achieved a 90 % conversion of the fatty acids within 30 min of reaction and at 270 °C in less than 60 min. The second step, the methyl esterification of fatty acids to FAME, achieves a 90 % of conversion at 270 °C in 30 min of reaction at 200 bar with a 1,8:1 volume relation of MeOH/Fatty acid. During this study, it was also demonstrated that a little back-feeding of the FFA formed in the hydrolysis process, helps to increase the conversion of TG to FFA at lower conditions. For example, without back-feeding a conversion of 90 % is achieved at 290 °C/150 bar in 40 min, and with back-feeding 94 % of conversion is achieved at 270 °C/150 bar in 25 min. Establishing again the autocatalytic phenomenon of fatty acids acting as acid catalyst.

ALMARALES *et al.* (2012), REYES *et al.* (2012) and CHENARD DIAZ *et al.* (2013) studied the synthesis of methyl esters of oil obtained from microalgae biomass. It was found that microalgae is a feasible raw material to obtain biodiesel of good quality. In CHENARD DIAZ *et al.* (2013) research, the reactions were performed in an autoclave reactor of 300 mL. Reaction conditions for hydrolysis of the oil obtained from the biomass were: temperature 300 °C, biomass concentration 20 %, agitation 400 rpm (revolutions per minute) and 1:5 molar ratio oil/water. For the esterification process a 3:1 alcohol/fatty acid molar ratio, 20 % of catalyst at 200 °C and 500 rpm for an hour achieving a conversion to methyl esters of 93 %.

Another study carried out to synthetize biodiesel by hydroesterification is presented by JU *et al.* (2013). Using refined soybean oil under subcritical water and methanol showed a conversion of 96,4 % in 4 h. On the same study, soybean oil with a 9 wt% of water content showed a 92,6 % of conversion. The temperature used in this system was 175 °C with a 35 bar of pressure (nitrogen) to ensure the subcritical condition of water and methanol. It was determined that FAME conversion increases with the decrease of water content being 1:5 wt% oil/water content the proportion with better results. To conclude, methanolysis and hydrolysis reactions occurs simultaneously in the presence of subcritical water, where sub-critical water acts as a catalyst for a hydrolysis reaction.

Using the same two-step method, MICIC *et al.* (2015) optimized the reaction parameters on the effectiveness of hydrolysis. The parameters studied were reaction time, temperature, water/oil molar relation and pressure. The results of the optimization showed that high FFA yields are obtained with the increase of temperature from 200 to 250 °C, however, for higher temperatures, no difference on the yield was observed. Therefore, 250 °C was defined as the optimal temperature for hydrolysis. At such temperature the optimal water/oil molar ratio was 20:1, a higher ratio did not increase the FFA yield, on the contrary, slowed down the reaction rate. As for pressure, it was found that the pressures studied (80 and 120 bar) had no influence on the FFA, nonetheless, the increase in pressure reduced the time needed to achieve maximum yields, and 120 bar was selected as optimal from the economic point of view. At 90 min under the optimized parameters was achieved nearly 100 % of yield for the sunflower seed oil. It was concluded that the highest impact for subcritical hydrolysis on the FFA yields are reaction time, followed by temperature and water/oil molar ratio. This study also confirmed that the two-step procedure have higher FAME yields at milder conditions as compared to the single-step transesterification procedure.

DOS SANTOS *et al.* (2018) studied the biodiesel production by subcritical/chemical hydroesterification of crude palm oil. During the study the optimal conditions found for the hydrolysis process were 100:1 water/oil molar ratio, 700 rpm at 250 °C for 120 min. Under the mentioned conditions the yield of FFA was 86 wt%. The glycerol produced in the reaction has a higher aggregation value since is from free contamination. The esterification process was performed using methanol obtaining a conversion to FAMEs of 99,1 %. In this research, it was found that the produced biodiesel comply with the quality control specification of resolution ANP No.45.

3.3.1.3 Catalytic hydrolysis

Catalytic hydrolysis can be carried out by three different type of catalyst: homogeneous, heterogeneous and enzymes. The aim of the catalyst is to increase the conversion of fatty acids and the selectivity towards the desired products. The use of catalyst does not affect the final equilibrium point but helps the reaction to reach this equilibrium in a shorter period of time (ITTNER, 1936).

- Enzymatic hydrolysis

Enzymes are biological catalyst of high performance and considering its biodegradable nature are less polluting. One advantage of this process is the high selectivity towards the desired product (POURZOLFAGHAR *et al.*, 2016). Enzymatic reactions are conventionally carried out at mild conditions (20-40 °C) and atmospheric pressure (MACHADO, 2013). In this case, the aqueous solution of lipase gets in contact with the oil forming a liquid-liquid dispersion. Nonetheless, this catalysis requires a long-running operation and is a bit more expensive than the other ones (SATYARTHI *et al.*, 2011; POURZOLFAGHAR *et al.*, 2016). Another disadvantage, is that enzymes are susceptible to deactivate in the presence of alcohol in hydroesterification processes, and require a precise control of the pH (CAVALCANTI-OLIVEIRA *et al.*, 2011; SANTOS *et al.*, 2015). Additionally, some typical components of vegetable oil as phospholipids can be inhibitors of lipase activity (ZENEVICZ *et al.*, 2017).

To show the versatility of the hydroesterification process with enzymes DE SOUSA *et al.* (2010) studied the hydrolysis conversion of different types of oils (crude, refined and waste oil) using a lipase extracted from nuts seeds. The reaction conditions were the same for all oils tested, 10 %w/v of substrate, 10 % w/w of lipase, pH of 8,0 at 40 °C during 2 h using Tris-HCl (hydrochloride) as buffer. For oils like soy, palm, crude palm and physic nut the FFA conversion were over 90 %, showing a remarkable capacity of the enzyme on hydrolyzing triglycerides. TALUKDER *et al.* (2010) studied the conversion of waste cooking oil to biodiesel. The lipase used to hydrolyze the oil was *Candida rugosa.* Complete conversion was obtained at a ratio of 1:1 (v/v) water/oil, 5 mL of lipase, 5 g of oil at 30 °C for 10 hours. The FFA obtained on the hydrolysis process was followed by esterification with ethanol using Amberlyst 15 catalyst, obtaining a 98 % yield.

CAVALCANTI-OLIVEIRA *et al.* (2011) studied the hydroesterification of soybean oil for biodiesel production. The hydrolysis step was carried out using the Lipase *thermomyces lanuginous* as catalyst. The highest conversion to FFA was 89% with a volumetric water/oil ratio of 1:1, 2,3 %v/v of lipase at 60 °C during 48 h. For the esterification step, with the use of methanol and niobic acid as the catalyst, the yield obtained was 92 %.This study showed a great conversion under low concentration of lipase, high oil content and no use of buffer, organic solvent or emulsifier. However, the reaction time required to achieve high conversion is large.

POURZOLFAGHAR *et al.* (2016) made a review on enzymatic hydroesterification process, reaching the following conclusions: use of different oils, especially low-cost feedstock, are suitable through this process; each feedstock and enzyme need unique process conditions;

the range of temperature for the hydrolysis process are typically 30-60 °C, with a pH range of 4,5-9,5; the most common lipase used for hydrolysis of oils is *Candida Rugosa*; the temperatures range for enzymatic esterification are 25-65 °C and the most common enzyme for esterification is Novozym 435.

Different studies hydrolyzing frying oil were performed by ZENEVICZ *et al.* (2017) using an ultrasound bath-assisted system. The enzymatic hydrolysis was conducted at different conditions. The optimal condition was using 1:20 molar ratio (oil/water), ultrasound power of 132 W, 40 °C, 300 rpm, 10 wt% Lypozime for 2 h. During the study was observed that ultrasound bath helped to increase the FFA content, being under the tested conditions 60 % for soybean oil and 61 % for frying oil. After hydrolysis, enzymatic esterification with Novozym achieved 83 % conversion to ethyl ester in 7 min and 94 % of conversion after 28 min. Both experiments suggest that low cost raw material are a good alternative for production of biodiesel using enzymes.

MACHADO *et al.* (2017) researched the enzymatic hydrolysis using the low-cost enzyme extracted from castor bean seed. As feedstock macaw pulp a high acid oil (45,81 %FFA), which could not be used in conventional transesterification. The conditions for the hydrolysis process were 35 °C, pH 4,5, 25 % oil/water mass concentration and stirring of 1000 rpm. After 2 h of reaction, was obtained a yield of 83 % of FFA. Esterification part showed a 97 % conversion to biodiesel. This study shows a promising solution for high acid value oils to produce biodiesel.

- Homogeneous hydrolysis

Homogeneous catalysis occurs when the catalyst is in solution with at least one of the reagents. Normally, this reaction is carried out by an acid catalyst such as sulfuric acid, hydrochloric acid, phosphoric acid or sulfonic acid (SANTOS *et al.*, 2015). Basic catalyst can also be used; however it could cause saponification of the fatty acids, reducing the operational yield (LAM *et al.*, 2010; MACHADO, 2013). One of the disadvantages of homogenous catalyst is the difficulty to separate it from the product and reuse it. Furthermore, homogenous catalyst can be toxic and corrosive when compared with heterogeneous catalyst. The most famous and well used hydrolysis process with homogeneous catalyst is the Twitchell process. A strong homogenous acid catalyst called ‘Twitchell reagent’ consisting of aromatic hydrocarbons, oleic acid, and concentrated sulfuric acid, is used to speed up the rate of reaction. Regardless of the low reaction conditions (100°C), the use of a huge amount of energy, long reaction time (12-

24 hr) and low conversion (80-85%) make the process less attractive and more expensive (ITTNER, 1936; LOGAN *et al.*, 1978; SATYARTHI *et al.*, 2011; ANNEKEN *et al.*, 2012).

The patent for Hydrolysis of triglycerides by LOGAN *et al.* (1978), presents a hydrolysis process conducted with a strong acid catalyst, a displacing acid catalyst and water (0,5–8 % p/p being the optimal 2 %). It is specified that the displacing catalyst is used to solubilize the triglyceride in the water and should be a low molecular carboxylic acids catalyst (e.g., acetic acid, formic acid, acetic acid and propionic acid). It consists in a two steps process: first the triglyceride reacts with the displacing acid and water. It forms a water-soluble glyceride (esters form from glycerol and fatty acids). Then, the strong catalyst acts to catalyze the reaction between the water-soluble glyceride with water to produce glycerin and FFA. The preferred strong catalyst is sulfuric acid. The reaction temperatures are 120-160 °C and the pressure from 1-8,6 bar, 90 % of conversion is achieved within less than four hours of reaction.

LUO *et al.* (2014) reported the use of ionic liquid as catalyst for hydrolysis of oils. Different SO_3H-funtional Bronsted acidic ionic liquid with different nitrogen groups were studied. The ionic liquid presents properties of homogenous (e.g., without diffusion limitation) and heterogeneous (e.g., readily separable and reusable) catalyst, used extensively in transesterification process but not in hydrolysis. The reaction was carried out in a 250 mL batch reactor using a stirring rate of 1500 rpm. The operational conditions were: 180 °C, water/oil molar ratio of 10:1 and 8 wt% (of oil) dosage of catalyst. The ionic liquid butylcaprolactamium hydrogen sulfate $[HSO_3bCPL][HSO_4]$ achieved a conversion yield greater than 95 % at 6 h of reaction. It was also established that the catalytic performance of the ionic liquid remained unchanged after 6 cycles of recycling, showing this as a suitable alternative of hydrolysis reaction at mild conditions under homogeneous catalyst.

- Heterogeneous hydrolysis

Heterogeneous catalysis takes place when the catalyst is in a different phase other than the reagents. The catalyst is normally solid and usually metallic oxides. Different catalyst are reported such as metallic oxides, zeolites, metallic complexes, organic salts, ion-exchange resin etc. Catalyst can be synthetized in different structures, pore size and hydrophobicity, according to the polarity of the reactants. Some of the advantages are the easy separation of the product and the catalyst, and therefore its reuse in future reactions. However, this reaction requires higher pressures and temperatures to achieve the same yield as homogenous catalysis (SATYARTHI *et al.*, 2011; SANTOS *et al.*, 2015).

NGAOSUWAN *et al.* (2009) reported the use of solid acid catalyst for the hydrolysis of triglycerides. The catalyst used consisted in a tungstated zirconia (WZ) and solid acid composite Nafion resin nanoparticles supported on mesoporous silica (SAC-13). Tricaplyn (TCP) was used as a model compound representing triglycerides. The reaction was conducted at atmospheric pressure and 110-150 °C in a semi-bath reactor with continuous addition of water at low flow rates. Despite the uniqueness of the process, yields were low. Also, the acid catalyst system showed deactivation in recycling studies.

SATYARTHI *et al.* (2011), studied the catalytic activity for hydrolysis of different vegetables oil and animal fat using different solid acid catalyst. For the hydrolysis step for soybean oil, the catalyst with better conversion selectivity towards FFA was ZnO and H_2SO_4, however, the separation of such catalysts from the product was really difficult. The third better catalyst was Fe-Zn double-metal cyanide (DMC). In a batch reaction, complete conversion of the triglycerides to fatty acids was obtained, with a selectivity greater than 73 wt% for all the oils studied using the last mentioned catalyst. The reaction conditions were: temperature of 190 °C, autogenous pressure, 0,5 g of catalyst, 10 g of oil, molar ratio of oil/water 1:30 and a reaction time of 12 h in a 100 mL stainless steel reactor. This research shows a great conversion of triglycerides with high selectivity. SRINIVAS & SATYARTHI (2011) follows the prior research to produce biodiesel with the esterification of the FFA over the Fe-Zn DMC catalyst. The study showed to be efficient for the conversion of the feedstocks to biodiesel.

On ALVES *et al.* (2014) research, is presented the study of magnetic mixed iron/cadmium and iron/tin oxide nanoparticles as catalyst in biodiesel production from soybean oil. The performance of the catalysts were analyzed for the hydrolysis, transesterification and esterification process of the oil. The reactions were carried out in a 100 mL parr reactor under 800 rpm stirring a 200 °C. The catalyst with better efficiency in the hydrolysis of soybean oil was the iron/cadmium with a conversion higher than 80 % in 4 h reaction, in comparison with 40 % in 4h for the other catalyst. For the transesterification process the best catalyst was also the iron/cadmium, possibly because of the large density of Lewis acid sites on the catalyst. For esterification process, both catalysts presented good yields (>80%) on the conversion of fatty acids to FAME. Additionally, it was demonstrated that iron/tin oxide catalysts did not present significant change on its structure even after four times of recycling. On the contrary, Iron/cadmium oxide presented considerable changes in the structure after the reaction.

MOWLA *et al.* (2018a) studied the influence of different parameters on the hydroesterification reaction using different zeolites (acidic heterogeneous catalyst) and feedstocks. It was found that increase on temperature (90-250 °C) enhances the level of

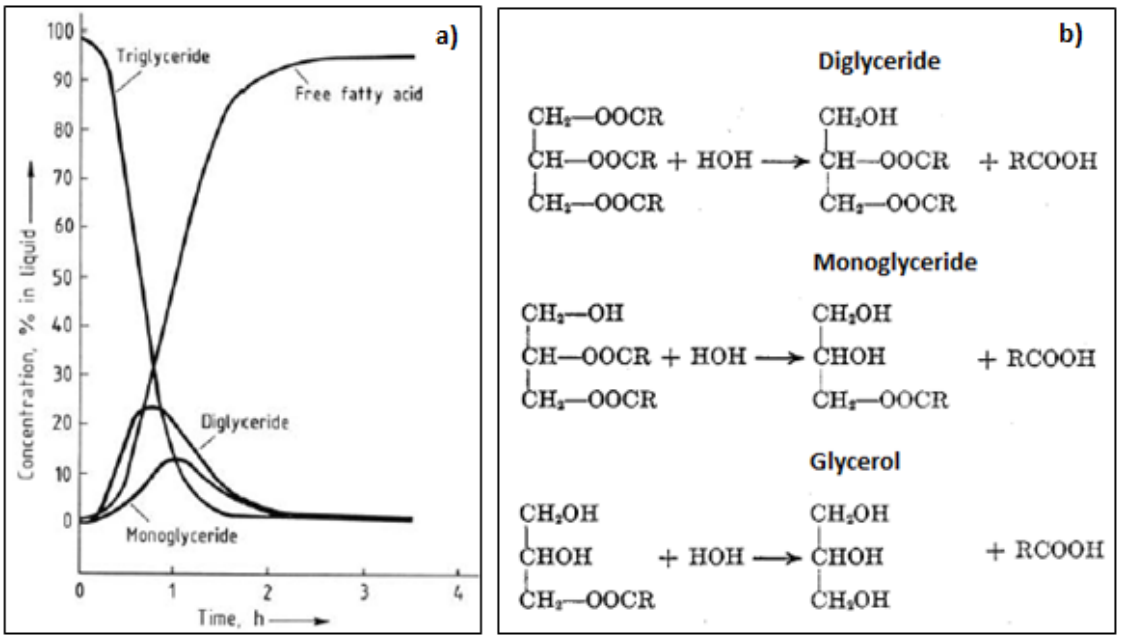
conversion. On the other hand, the incidence of catalyst at high temperatures (250 °C) does not impact the conversion when compare to non-catalytic test. Concluding that, at low (100 °C) and high (250 °C) temperatures, the highest conversion is achieved at 5% (w/w oil) of catalyst. The main difference for both temperatures is the time of reaction necessary to achieve the highest yield, being for 100 °C 240 min and for 250 °C 30 min. The stirring rate was found to have an important influence. The rates studied were 60-600 rpm, where from 60-250 rpm the conversion of oil seemed to enhance, but for rates over 250 rpm, conversion level seemed to be inhibited. Concerning to water concentration, were studied various oil-water ratios, 1:1 to 5:1 v/v. The best ratio was between 2:1 and 3:1 v/v for the zeolites studied. Under the optimized parameters the rate of conversion to FFA was lower than 60%. This study concludes that inadequate water concentration results in incomplete conversion during hydrolysis and that reaction temperature and stirring rate are the primary factor to achieve an optimized catalytic performance. MOWLA *et al.* (2018b) also concluded that zeolite-catalyzed hydroesterification showed to be successful for low-quality waste oil feedstock at temperatures lower than 100 °C.

3.3.1.4 Reaction scheme

Reactants in the hydrolysis of fats/oils form a heterogeneous system are composed of two phases: (1) disperse-aqueous phase formed by water and glycerol, and (2) the homogeneous-lipid phase containing glyceride and fatty acid (ITTNER, 1936; MILLS & MCCLAIN, 1949; SAKA, 2006). A third phase can be found in the case of heterogeneous catalysis.

Hydrolysis occurs as a homogeneous reaction by dissolving water in the lipid phase. As shown in Figure 5a through reaction time, triglyceride concentration starts decreasing, and mono and diglyceride start increasing along with FFA up to a certain point, where mono and diglyceride concentration commence to decrease. In about two hours reaction most of the glycerides are converted into FFA, under the studied conditions. Figure 5b represents how the reaction takes place in several stages via partial glyceride (diglycerides and monoglycerides) (ANNEKEN *et al.*, 2012). First, one mole of triglyceride reacts with one mole of water and forms one mole of fatty acid and one mole of diglyceride, then the diglyceride is converted into monoglyceride and next into glyceride. At the end of the reaction there is a high concentration of free fatty acids, corresponding to three moles of free fatty acids and one of glycerol for every mole of triglyceride reacted with three moles of water.

Figure 5. Reaction scheme of hydrolysis reaction

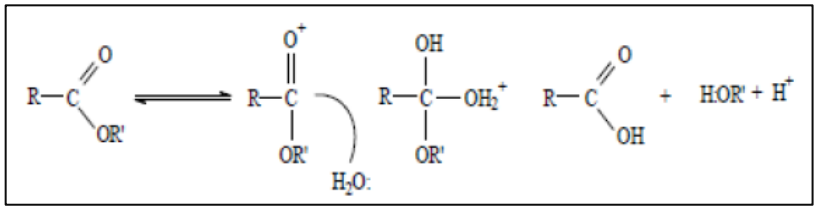


a) Typical course of hydrolysis reaction at 235 °C and 35 bar using 1 part oil and 2 parts water. (ANNEKEN *et al.*, 2012)

b) Scheme of hydrolysis of fatty oils. Adapted from (SUEN & CHIEN, 1941)

Since acid hydrolysis is the focus of this work in Figure 6 is the representation of its mechanism. The protons connect with the oxygen from the carbonyl and become vulnerable to nucleophilic attack from water.

Figure 6. Acid hydrolysis mechanism



(ACOSTA, 2014)

To ensure a high conversion of triglycerides to free fatty acids is important to take into account the parameters with more impact on the yield of reaction, regardless the type of hydrolysis.

3.3.1.5 Parameters influence

Hydrolysis of vegetable oils/fats is an endothermic reaction. The extent of hydrolysis increases with an increase in temperature (HOLLIDAY *et al.*, 1997; MINAMI & SAKA, 2006; ALENEZI *et al.*, 2009). Up to 100 °C, fat hydrolysis is very slow or null. PINTO & LANÇAS (2006) demonstrated that at low temperatures, the speed and yield of the hydrolysis are practically none as a result of the low solubility of water on the triglycerides. While at temperatures above 210 °C, the yield can be higher than 80 %. Further, at higher temperature and pressure, the solubility of the two (aqueous and lipid) phases increases and, thereby, enhances the reaction rate.

One of the main factors for obtaining a high yield of FFA is the adequate water-oil ratio. This is the limit factor of the reaction, since the yield in equilibrium is independent of the temperature or catalyst and is determined by the water-oil ratio (ITTNER, 1936; LOGAN *et al.*, 1978). However, a huge excess of water does not enhance the conversion level of oil and can act adversely on the extent of hydrolysis (MICIC *et al.*, 2015; MOWLA *et al.*, 2018a). Another important fact is that water should be demineralized because hardness reduces catalyst efficiency (ANNEKEN *et al.*, 2012; SANTOS *et al.*, 2015).

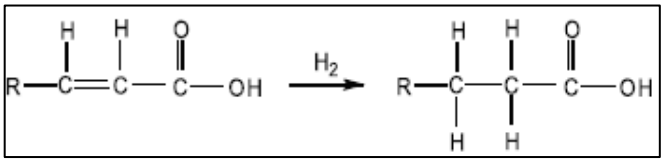
Stirring rate is also an important parameter. An adequate stirring rate minimize the mass transfer limitation, however, the effectiveness of stirring is reduced if the stirring speed increases above the optimum level (MOWLA *et al.*, 2018a). Moreover, that the addition of FFA at the beginning of the hydrolysis reaction helps to speed up the rate and lower the reaction conditions, since FFA acts as an acid catalyst (MOWLA *et al.*, 2018b).

The fatty acid obtained is used as raw material in the manufacture of different products. However, the unsaturation of some fatty acids' chains makes them susceptible to oxygen attacks, which can cause rancid odor and therefore problems in the product. To minimize or eradicate those problems and improve the characteristics of the product, it is necessary to saturate those multiple bonds via hydrogenation. The aim of this study is the production of saturated free fatty acids.

3.3.2 HYDROGENATION OF OILS AND FATTY ACIDS

Hydrogenation, or “hardening”, is a well-known process to saturate organic matter. It consists on the addition of hydrogen (H_2) in the double bonds of the unsaturated triglycerides or fatty acids. The reduction of the carbon-carbon double bonds results in the reduction of the iodine value (IV). The process improves the stability of unsaturated compounds and it is used in the manufacturing of a great number of products such as, margarine, shortenings and other edible fats, lubricants, cosmetics, soaps, and more. The reduction of the IV in hydrogenation improves the odor and color, gives better oxidative stability and changes the melting and solidification characteristics of the treated oils (SCHOKKER, 1982; BELKACEMI *et al.*, 2006; CHENG *et al.*, 2012). Figure 7 represents a fatty acid molecule with one unsaturation and the saturation of the molecule after the hydrogenation reaction.

Figure 7. Hydrogenation of fatty acids



(NEUZA, 2009)

Hydrogenation involves three phases: gas phase (Hydrogen), liquid phase (triglycerides and dissolved hydrogen), and the solid phase (metallic catalyst)(ALBRIGHT, 1963). To carry out this reaction it is necessary to have a catalyst with selectivity towards hydrogenation. The most active catalyst for this type of reaction are platinum and palladium. However, because of the high price of noble metals, the most commonly used in industry is Nickel (WISNIAK & ALBRIGHT, 1961; ALBRIGHT, 1963; HASHIMOTO *et al.*, 1971; BROECKER *et al.*, 1975; HASTERT, 1979; LIST & KING, 2016).

The majority of the unsaturated fatty acids present in the vegetable oil and animal fat are *cis* configuration (ZIEVERINK, 2007). If unsaturated fatty acids leave too fast the surface of the metallic catalyst (short retention time), the hydrogenation reaction is not completed and double bonds may be shifted to other positions on the carbon chain or adopt another structure, which is called isomerization (WISNIAK & ALBRIGHT, 1961; FERNÁNDEZ *et al.*, 2007; AIKEN & & ZHENG, 2018). It also occurs when a low concentration of hydrogen is present on the catalyst surface, and the reaction cannot be completed. Hydrogenation and isomerization process occur simultaneously and both on the catalyst surface (ALBRIGHT, 1963;

SCHOKKER, 1982; FREY, 2008). According to BAILEY (1949), WISNIAK & ALBRIGHT (1962) and other authors, the transfer of hydrogen from the gas to the liquid phase is often the single most controlling step. In the other hand, mass transfer resistance seems to be negligible in runs at high agitation rate (ELDIB & ALBRIGHT, 1957; WISNIAK & ALBRIGHT, 1962; ALBRIGHT, 1963)

There are two types of isomerization: geometrical and positional isomerization. Geometrical is a *cis-trans* isomerization caused by a partial-hydrogenation. It has been found that, at temperatures above 200 °C, *cis* double bonds are converted into *trans*-isomers and, according to ALBRIGHT (1963), the *trans/cis* ratio is 2:1. Higher amounts of trans-isomers increases the softening temperature and gives a higher thermodynamic stability (KOCSISOVÁ *et al.*, 2006). It also important to highlight that the *Solid Fat Content* test increases not just with the increase of saturation of the double bonds, but also with the amount of *trans*-isomers. This means that *trans*-isomers have a high fusion point than *cis*-isomers as shown on Table 5. Positional isomerization occurs when unsaturated double bonds change the position along the fatty acid chain. The degree of positional or geometrical isomerization can be predicted in the concentration of hydrogen at the catalyst surface (ALBRIGHT, 1963).

Table 5. Fusion point of C18 fatty acids

Fatty acids	**Fusion point (°C)**
18:0	70
18:1 (9 cis)	16
18:1 (9 trans)	45
18:2 (9c, 12 c)	-5
18:2 (9t, 12t)	29
18:3 (9c, 12c, 15c)	-11
18:3 (9t, 12t, 15t)	30

(GUNSTONE & NORRIS, 2013)

Trans-fatty acids are side products of catalytic hydrogenation that can cause health problems since human body does not recognize them. The importance of these transformations depends mainly on the catalyst selectivity, hydrogen delivery, temperature, pressure and agitation. The modification of the reaction conditions can result in higher hydrogen concentration on the catalyst surface and, therefore, a reduction on trans fatty acid level (BEERS, 2007). Isomerization and hydrogenation are strongly influenced by temperature. The higher the temperature the lower the saturate formation and the higher the trans-isomer formation. The lower the amount of trans-isomers, the higher the amount of saturates (BEERS, 2007).

Furthermore, the speed of hydrogenation depends on the content of impurities in the oil/fat or fatty acid. The most detrimental components are soap and sulfur contaminants and proteinaceous material (HASTERT, 1979). To pursue an adequate hydrogenation process, the feedstocks needs to be free from those contaminants usually removed through distillation, especially when low iodine is desired. Because of the amount of reaction steps, the interfacial area of the catalyst and the degree of agitation are highly relevant.

Hydrogenation process is normally evaluated by iodine value, that gives an idea of the degree of saturation of the oil (NEUZA, 2009). According to ZIEVERINK (2007) and GÓMEZ (2009) the degree of hydrogenation will depend on the type of application for which it will be used.

- Brush hydrogenation: used to increase the shelf-life of a liquid oil. Only linolenic fats are hydrogenated.
- Partial hydrogenation: the reaction stops when the desired balance of saturates and *trans*-isomers is reached. It is aimed to obtain selectively monounsaturated fatty acid groups (HASHIMOTO *et al.*, 1971). The iodine value can oscillate between 50 and 100 (BEERS, 2007; CHENG *et al.*, 2012). Its purpose is to obtain a sharp melting point, flavor stability and firmness at room temperature (ZIEVERINK, 2007). The products are mostly used for soap formulation and food industry (EVONIKCATALYST, 2016b).
- Total hydrogenation: the objective is to saturate all fatty acids until obtaining an iodine value close to zero. Fusion point is usually higher than 60°C, making it not suitable for food purposes. Products with lower iodine value have a large number of industrial applications i.e. manufacture of tires, lubricants, greases, fatty alcohols and cosmetics (EVONIKCATALYST, 2016a).

Another important term in hydrogenation process is the induction period. It is defined as the time at which the extrapolated straight line coincide with the initial iodine value (HASHIMOTO *et al.*, 1971). It has been reported induction periods varying from 10-80 min for batch runs at 100-130 °C. The increase in temperature leads to the decrease of the induction period. At temperatures over 160 °C, the induction period is low or inexistent (ALBRIGHT, 1963).

3.3.2.1 Hydrogenation reaction scheme

Since hydrogenation and isomerization occurs simultaneously and both on the catalyst surface, it is important to know the steps involved during the hydrogenation process. Such mechanism is represented in Figure 8 and it is listed as follows:

(a) First the hydrogen is transferred from the gas to the liquid phase and then the reaction process starts in the metallic catalyst surface.

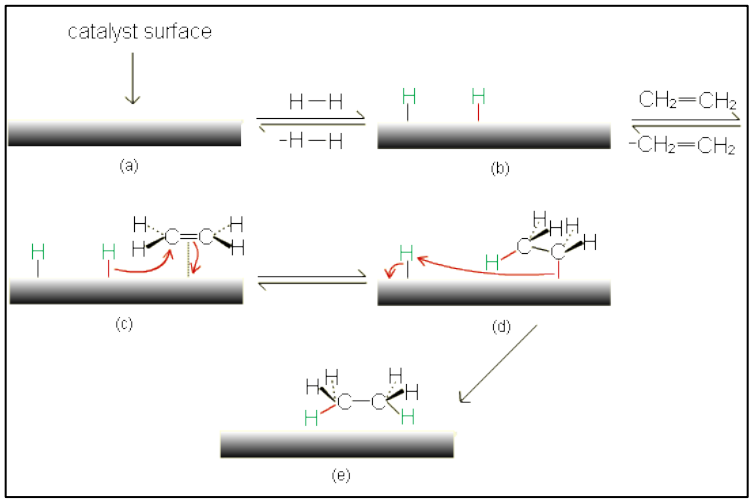
(b) The catalyst adsorbs the hydrogen atoms over the metal surface and then it is dissociated into two hydrogen atoms (H*)

(c) The alkene is also absorbed in the catalyst surface

(d) After the reactants are transferred to the catalyst surface, chemical reactions (adsorption, surface reactions, desorption) take place. The surface reaction process partially breaks the C=C bonds and the H-H connections. Then, hydrogen insertion into the carbon double bonds occurs.

(e) Afterwards, the saturated alkane produced is desorbed, leaving the surface of the catalyst free to absorb new reagent molecules and the product of the reaction is transferred from the catalyst surface to the main body liquid.

Figure 8. Catalytic hydrogenation mechanism

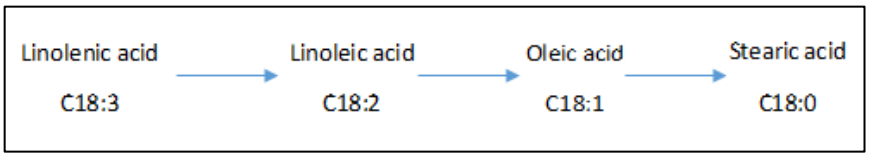


(CHEMGAPEDIA, 2018)

The product can be a fully hydrogenated acid group, such as stearic acid, or a monounsaturated acid group. However, the monounsaturated group can remain in the catalyst surface until full hydrogenation or isomerization and then transferred to the liquid phase. According to ALBRIGHT (1963) and ANNEKEN *et al.* (2012), polyunsaturated fatty acids

groups have more selectivity than unsaturated ones during the reaction process. Polyunsaturated tends to be more strongly adsorbed than monounsaturated. When high concentration of hydrogen exists on the catalyst, it will tend to react with the first double bonds that approaches the catalyst, this will be random and non-selective. On the other hand, if hydrogen concentration is low, the selectivity will be towards polyunsaturated fatty acid groups, increasing the isomerization. The following scheme, Figure 9, represents the order of selectivity hydrogenation reaction.

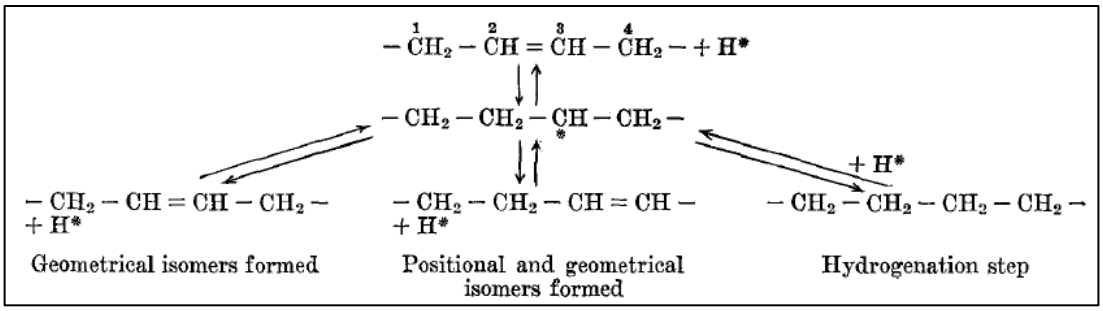
Figure 9. Selectivity in hydrogenation reactions



(SCHOKKER, 1982)

In Figure 10, the isomerization and hydrogenation process is represented. When the hydrogen molecule is dissociated on the catalyst surface to hydrogen atoms, one of the activated atoms (H*) attacks the double bond to produce an unstable partially unsaturated complex. High hydrogen concentration on the surface will lead to complexity to react with another hydrogen atom and complete the hydrogenation. Nonetheless, if the hydrogen concentration is low, the hydrogen atom will, most likely, dissociate from the complex to reform the double bond and isomerization will take place.

Figure 10. Isomerization and hydrogenation



(ALBRIGHT, 1963)

3.3.2.2 Catalyst for hydrogenation

Hydrogenation of unsaturated fatty acids or triglycerides is commonly carried out by heterogeneous catalysis. Solid catalyst, liquid-phase reactants, and products forming at least two phases, characterize this type of catalysis. Solid catalyst are highly important in many chemical processes, since it improves selectivity, easy catalyst separation from reaction mixture, and the possibility of reuse in further reactions. The selection of an adequate catalyst is of extreme importance because it ensures the desired hydrogenation with a minimum of isomerization taking place. As explained before, isomerization is a side reaction to be avoided.

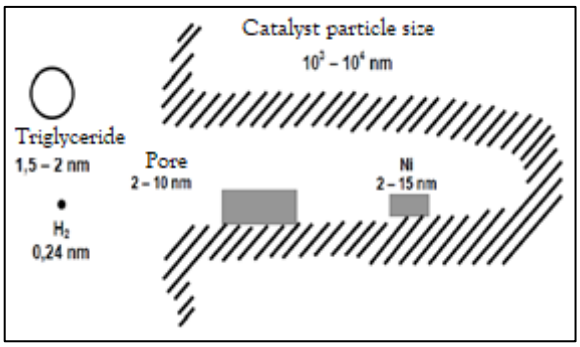
Cobalt, copper, ruthenium, palladium, platinum are more active catalyst but, due to its price, are used in a limited extend (SIMS, 1952; ALBRIGHT, 1963). The performance/price ratio of nickel catalyst make it more suitable for industrial processing (DEUTSCHMANN *et al.*, 2009; GUNSTONE & NORRIS, 2013; DE *et al.*, 2016; KORDULIS *et al.*, 2016).

Supported nickel catalyst find wide application in many hydrogenation processes (BARTHOLOMEW & FARRAUTO, 1976; LIST & KING, 2016). The goal of using supports is the increase of the active phase dispersion, the better control of the porous structure, improvement of mechanical strength, sintering prevention and to assist the catalysis. Silica, alumina and silica-alumina are typical supports of nickel catalyst applied on hydrogenation processes (MCARTHUR & LINDA, 1980; FREY, 2008). Silica-supported nickel catalysts are used on hydrogenation, deoxygenation, methanation, reforming, and hydrocracking processes (HERMIDA *et al.*, 2018). On the other hand, alumina (Aluminum oxide) is highly used as support for noble metals and Nickel on hydrogenation of fats and oils (ERTL *et al.*, 1997; DEUTSCHMANN *et al.*, 2009).

In any case, the catalyst is prepared by the precipitation of nickel salt on the support. After the impregnation of the support with the nickel salt, washing, drying, calcination, and final reduction to Ni^0 is performed, with hydrogen at elevated temperatures. Because of the pyrophoricity of the product, an immersion in a protective medium, such as fully hardened vegetable oil, is necessary.

In Figure 11 by BALAKOS & HERNANDEZ (1997), is represented the relative size of components of the reaction. With the figure is possible to have an idea of the catalyst particle size, pore size and molecule size.

Figure 11. Relative size of reaction components



Adapted from: (BALAKOS & HERNANDEZ, 1997)

Low solubility of hydrogen on the oil, high reagents molecule size and the high activity of the nickel catalyst, make this processes to be controlled by diffusion. Small size particles are desired, but too small would result in poor filtration. The pore diameter of the carrier must be large enough to allow transport of fatty acid/triglyceride molecules to the nickel crystallites (ANNEKEN *et al.*, 2012). Considering that the reactions occurred on the catalyst surface, a high surface area is crucial to achieve high performance.

Industrially, different Nickel catalyst are used, as Raney Nickel and Nickel *Kieselgurhr* (mixture of silica, alumina and iron oxide). Generally on the Nickel *Kieselgurhr* catalyst the proportion is: 25% Nickel, 15% *kielselgurhr* and 60% of fat protective layer (ANNEKEN *et al.*, 2012; LIST & KING, 2016; RASE, 2016). On the other hand, Raney nickel is a porous catalyst. It is made of 50% aluminum and 50% nickel, a Nickel-Aluminum alloy, treated with a concentrated solution of sodium hydroxide (NaOH) (ALBRIGHT, 1963). The NaOH dissolves the aluminum in sodium aluminate form, leaving a porous Nickel (OLIVEIRA, 2008). Raney nickel is available as a slurry or in pellet form protected with a fat layer. Commercially the catalyst has an average Ni surface area of 200-600 m^2 per gram of catalyst (RASE, 2016).

One of the advantages of a heterogeneous catalyst use is that it can be reused several times. However, the activity decreases with time as the active sites are poisoned or "wear out." Since the triglycerides and hydrogen often contain poisons, the continuous use of the catalyst may increase poisoning. Hence, the refining and bleaching steps for the oils, and the purification operations for the hydrogen are important regarding catalyst activity and performance (ALBRIGHT, 1963). When catalyst poisoning occurs, the rate of hydrogenation is not the only affected, selectivity and isomerization may also change.

Some nickel catalyst are susceptible to poisoning. Some nickel poisons reported in the literature are: carbon monoxide, sulfur, phosphorus, halogens, soap and free fatty acid

(DROZDOWSKI & ZAJAC, 1977; BARTHOLOMEW, 1987; LIST & KING, 2016). Whereas poisoning by carbon monoxide is reversible in the sense that nickel carbonyl is unstable (GOMES *et al.*, 2014). However, the other substances may irreversible. Some cases have been reported where nickel/nickel oxide and the carboxylic group of fatty acid react and result on nickel soap. Nonetheless, to reduce soap formation, the reaction needs to be carried out at high pressures (ANNEKEN *et al.*, 2012; EVONIKCATALYST, 2016a).

3.3.2.3 Hydrogenation application

The first hydrogenation dates 1897 by Wilhelm Norman (HASTERT, 1979; ZIEVERINK, 2007), the discover was a result of an unsuccessful experiment to make nickel carbonyl by the addition of ethylene to nickel. The analysis of the result showed that nickel decomposed the ethylene into carbon and hydrogen, and such hydrogen hydrogenated the remaining ethylene to ethane. WILHELM (1903) created the first patent for liquid phase hydrogenation using nickel as catalyst, instead of platinum or palladium. The objective was to reduce the iodine value as much as possible, as fast as possible and as cheaply as possible.

ELDIB & ALBRIGHT (1957) used a semi-batch reactor in the hydrogenation of cottonseed oil. The effects of operating variables such as temperature (115-160 °C), pressure (1-10 bar), nickel catalyst concentration (0.03-0.15%) and agitation (550-1760 rpm) were examined. With the increase of temperature the IV decreased in less time, showing that the rate of reaction is linear with temperature. However, the formation of *iso*-oleic acid seemed to increase slightly with temperature. The influence of pressure on the hydrogenation rate showed to be directly proportional, as at the highest pressure studied (10 bar) the iodine vale was reduced from 105 to <35 in less time (<70 min) when compared to lower pressures (4 bar - >110 min). Additionally, the selectivity and isomerization decreased with the increase of pressure from 1 to 7 bar, while at pressures higher than 7 bar, it showed small impact. It was also found that the higher the catalyst concentration, the faster and the lower the IV was obtained, being also directly proportional to the reaction rate. The effect of agitation seemed to be significant for stirring rates up to 1175 rpm on reducing the. Agitation over 1175 rpm showed same selectivity and isomerization, while low agitation resulted in increase of the isomerization. WISNIAK & ALBRIGHT (1961) investigated the same effects under higher pressures (20-103 bar). It was found that with the increase of the pressure the selectivity and isomerization decreases. At such high pressure, the variation on temperature had no effect on selectivity and

just a small effect on isomerization. However, with the increase of temperature and pressure the rate of hydrogenation also increased.

HASTERT (1979) gathered different studies from different authors on the incidence of the reaction conditions in fatty acids and triglycerides hydrogenation. At the constant temperature of 216 °C and 0.02% nickel, the incidence of pressure on the reaction rate of distillated tallow fatty acid and distillated oleic acid is inverse, meaning that the highest the pressure, the lowest the IV is obtained in less time. However, after a certain pressure (>21 bar) the advantage is discernible. It was also established that the increase of temperature increases a reaction rate up to an optimum temperature, but after that level the effect caused is contrary. The optimum temperature varies for every fatty acids but it is generally from 180-210 °C. In the other hand for triglycerides such temperature is usually higher. At low stirring rates as (750 rpm) the IV reduction is minimal while for higher rates (900 to 1000 rpm) the maximum rate and lower IV is reached. Nevertheless, agitation >1000 rpm, showed no difference on the reaction rate. As for feedstock purification and the more pure the feedstock is the lower the IV can get.

HSU *et al.* (1986) studied the hydrogenation of canola oil (IV 115) under palladium black as catalyst for partial hydrogenation with low *trans*-isomers content. The reaction was carried out in a 300 mL parr reactor at an agitation rate of 830 rpm and 100 gr of oil. Temperatures from 30-90 °C, catalyst concentration from 80-560 ppm (part per million) and different pressures were studied. It was conclude that low pressures promote the *trans*-isomer formation, as well as high catalyst concentration and high temperatures. The optimal conditions for high partial hydrogenation and low *trans*-isomer formation was at 52 bar, 50 °C and 560 ppm. The product obtained had an IV=51 and 14% *trans* in 20 min. Latter, it was compared with a reaction with the catalyst supported, 5% Pd/C. It was found that the supported catalyst had a better activity but the *trans*-isomer formation was also enhanced. Summing up, palladium black showed to be a potential catalyst in hydrogenation of canola oil with low trans-isomer content.

As known, high pressures (60 bar) lead to lowering the *trans*-isomer formation, being however, unpractical on industrial scale. Lowering temperature also reduces *trans* isomerization, but decreases hydrogenation conversion. Because of that, BEERS (2007) analyzed the influence of variables of reaction on *trans* isomerization on hydrogenation of soybean oil (IV:120) using a Nickel catalyst especially developed for low hydrogenation temperatures. With the special catalyst, at low temperatures (40-60 °C) the amount of *trans*-isomers decreases, while the saturated level increases at the studied pressure of hydrogen (2-4

bar). It was also studied Pt catalyst. It showed the best hydrogenation (IV 70) at 5 bar and 200 °C with the lowest conversion to trans-isomers.

FERNÁNDEZ *et al.* (2007) evaluated the performance of nickel catalyst in sunflower oil hydrogenation under different operating conditions. The process variables studied were, reaction temperature (150-220 °C), hydrogen pressure (2,07-6,2 bar), amount of catalyst (500-1500 mg) and agitation rate (500-1800 rpm) for 1h in a 600mL parr reactor. All experiments were conducted in diffusional regime, and the aim of the study was to analyze the *cis*-isomers selectivity. It was determined that temperature is a variable very significant on controlling *trans*-isomers formation. Increase on temperature increased the *trans* formation, while the *cis* formation continued stable. Additionally, to obtain the same IV at low temperatures it is required more reaction time than with high temperatures. In the other hand, a high stirring rate leads to an improvement in the mass transfer and drives to a good dispersion of the catalyst and the gas in the reactor, improving the selectivity. However agitation over 1000 rpm showed to be invariant on the extent of reaction.

CHENG *et al.* (2012) studied eleven commercial catalyst based on Ni, Pd and Pt to hydrogenate cottonseed oil (IV: 115). The goal of this research was minimize the *trans* fatty acids production. The reaction was carried out at atmospheric pressure at 1200 rpm, two different temperatures (80 and 130 °C), for different reaction times (20 and 90 min), and different catalyst levels. Under the studied conditions, Pt catalyst generated the least amount of *trans* fatty acid, followed by Ni and then Pd. At 130 °C and 90 min of reaction was obtained the lowest IV (~10) for all catalyst. The catalyst level with better performance was 2% Ni, 0.5% Pt and 0.5% Pd. The behavior of the Ni (on solid support), Pd (5% on carbon) and Pt (5% on carbon) catalyst in the hydrogenation process at the better conditions was very similar, obtaining an stearic acid content at the end of the reaction of >75% and >25% of palmitic acid.

EVONIKCATALYST (2016a) is a known company in the production of Nickel based catalyst for hydrogenation of fatty acids and triglycerides. The catalyst is manufactured in pellets form, were the metal is dispersed in hydrogenated vegetable oil. For complete hydrogenation of fatty acids and triglycerides the catalyst contains 23% of nickel and for partial hydrogenation 17%. Palm fatty acid is hydrogenated at 14 bar, 180-195 °C and 80 min to obtain a product with IV <7. However, on different test using lower pressures (1,0-1,5 bar) hydrogenation rate was low, meaning that, the lower the IV desired, the higher the pressure needed.

Typical commercial hydrogenation is usually carried out in a semi batch reactor where hydrogen gas is bubbled in hot liquid vegetable oil at 150-200°C, usually under pressures of 0-

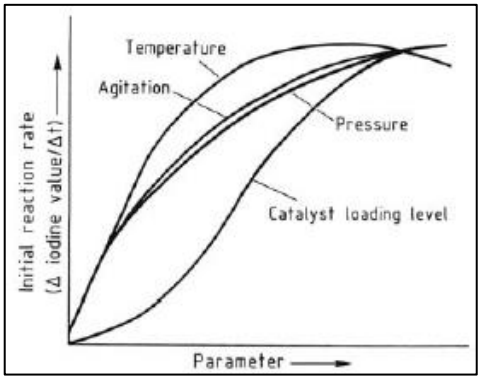
21 bar, catalyst concentrations 0,01-0,15% wt/wt Nickel and agitation (ALBRIGHT, 1963; KOBE *et al.*, 1991; BEERS, 2007; FERNÁNDEZ *et al.*, 2007; LIST & KING, 2016). To control hydrogenation process, some samples from the product are taken to analyze the iodine value obtained and determine the extent of hydrogenation.

3.3.2.4 Parameters influence

Different variables influence greatly on the hydrogenation rate. In Figure 12 is the representation of the different parameters and its incidence in the reaction rate, represented on the delta of iodine value and the time required to achieve it. Conditions that improve hydrogen dispersion of the catalyst surface reduce the selectivity and t*rans*-isomers formation.

From all literature reviewed and the graph, can be concluded that increase on temperature increases the reaction rate, until a range of 100-200 °C (BROECKER *et al.*, 1975; HASTERT, 1979; KOBE *et al.*, 1991; FERNÁNDEZ *et al.*, 2007). The increase of temperature above the optimum point increases selectivity and isomerization (BEERS, 2007). Increase in pressure and temperature improves the solubility of hydrogen in the oil. Consequently, with high concentration of hydrogen in the liquid phase, the better the contact of the reagents on the surface of the catalyst. In the other hand, the higher the pressure, the lower the IV obtain in less time and the less the selectivity and isomerization. Nevertheless, this phenomenon occurs just up to an optimal point (up to 25 bar (HASTERT, 1979)), where increase in pressure reduces the reaction rate.

Figure 12. Effect of operating variables on the reaction rate of fatty acid hydrogenation



(HASTERT, 1979; ANNEKEN *et al.*, 2012)

When hydrogen transfer is a controlling step, agitation increases the concentration of hydrogen at the catalyst surface, the rate increases and the selectivity and isomerization

decrease. When agitation is high, mass transfer resistance are negligible, yet, stirring rates greater than 1000rpm have no influence in the IV reduction and reaction rate (ELDIB & ALBRIGHT, 1957; FERNÁNDEZ *et al.*, 2007).

As the catalyst loading level increases, the reaction rate increases, except when hydrogen diffusion step is controlling. In that case the rate of hydrogenation per unit weight of catalyst decreases and the isomerization and selectivity increases (HSU *et al.*, 1986). If not, diffusion steps are controlling the overall rate (typically 0.02-0.1% of the weight of the oil) (DEUTSCHMANN *et al.*, 2009; ANNEKEN *et al.*, 2012; CHENG *et al.*, 2012).

Since the reactions occurs in the catalyst surface, it is important to have large surface areas for a given amount of catalyst, therefore small particle size are desired. However, the size should not be as small that can cause filtration problems during the treatment of the product. That is why the right balance between surface areas and porosities of the catalysts are generally more important than the catalyst loading level (HASTERT, 1979; LIST & KING, 2016).

The construction material of the reactor is also important. For hardening fatty acid, the material must be stainless steel, but for triglycerides not essential, but desired. The design pressure for the reactors for oil are 7 bar, and for fatty acids 34 bar (HASTERT, 1979). As expressed before, the quality of the oil is really important, especially when nickel is used as catalyst. Contaminants of the oil can obstruct the function of the catalyst and/or cause adverse reaction.

3.3.3 SIMULTANEOUS HYDROLYSIS AND HYDROGENATION

DÍAZ *et al.* (2014) studied the hydrolysis and hydrogenation of soybean oil. On this study the glycerol formed from the hydrolysis reaction is reformed into hydrogen, and such hydrogen is used as internal hydrogen donor to pursue the hydrogenation of the fatty acids. The catalyst studied were Ni/Al_2O_3, Ni/ SiO_2, Pd/Al_2O_3 and Pd/SiO_2. For the nickel based catalyst a concentration of 5-25% was used, while for Palladium catalyst a 1-5% concentration was added. Reactions were performed in a 300 mL batch reactor under the following parameters: 30 g of oil, 1:1 oil/water weight ratio, 3:1 molar oil/catalyst ratio, 290°C and stirring rate of 500 rpm. It was found that 25 wt% NiO/Al_2O_3 and 5 wt%PdO/Al_2O_3 catalyst had the better performance under the studied conditions. The lowest iodine value and highest FFA achieved for soybean oil was 11 mgI_2/g and 83% respectively.

SUGAMI *et al.* (2016) studied the simultaneous hydrolysis and hydrogenation of rapeseed oil in a batch reactor. One gram of rapeseed oil, 3 g of water and 0,05 g of catalyst

were placed inside the vessel. To pursue the reaction the conditions were: 270°C, 50 bar of hydrogen pressure, water, and Pd/C catalyst during 60 min. The yield of conversion was 98,4%.The remaining corresponded to diglyceride and monoglyceride.

3.4 CATALYTIC TRANSFER HYDROGENATION

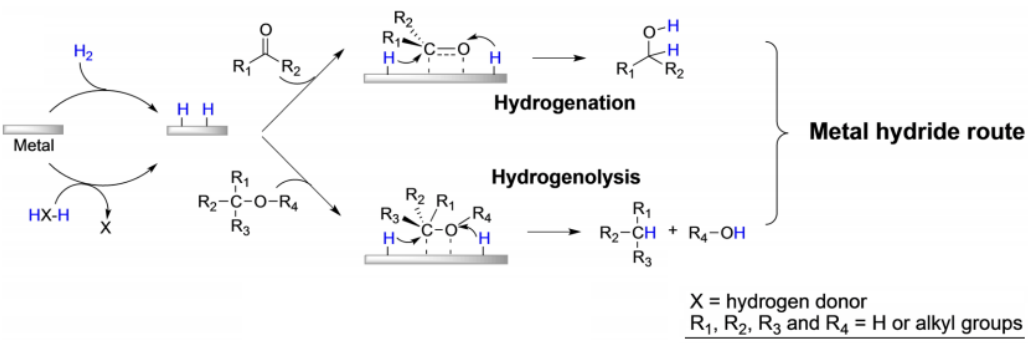
The main feedstock needed to carry out the hydrogenation process is molecular hydrogen, a flammable gas, difficult and dangerous to handle because of its hazardous properties. Along with the intrinsic characteristics of the gas, operational cost, infrastructure and logistical challenges on transportation and storage are other drawbacks of such feedstock.

Nowadays, industry is more concerned about searching new processes with low environment impact. One of the strategies is the substitution of feedstocks from fossil origin for renewable ones. Hydrogen is one of those feedstocks.

A suitable alternative studied over the years is the use of hydrogen donors from renewable sources (GONG *et al.*, 2014). Organic molecules offer a renewable alternative to molecular hydrogen. Such molecules act as hydrogen donor in the reduction of chemical bonds with the assistance of catalyst through a pathway known as catalytic transfer hydrogenation (CTH) (GILKEY & XU, 2016). Hydrogen donors are chemical components that when decomposed, generate the hydrogen needed for the hydrogenation process, working as internal hydrogen source.

Different mechanisms are proposed for hydrogen transfer. The most accepted in literature is metal hydride route. The metal sites are able to mediate the hydrogenation of the carbonyl group with formic acid as transfer agent. Figure 13, adapted from GILKEY & XU (2016), represents the mechanism.

Figure 13. Hydrogen transfer mechanism



adapted from GILKEY & XU (2016)

The most common metals used for this type of reaction are Ru, Ni and Pd (BRIEGER & NESTRICK, 1974). Metals can efficiently activate H-H, C=O, and C-H bonds. The CTH process starts by activating the organic hydrogen donor by the metal surface.

Some chemicals have been studied as potential hydrogen donors such as glycerol, ethanol, isopropanol, limonene and formic acid (KOBE *et al.*, 1991; WOLFSON & DLUGY, 2009; ROSANA DE SOUZA SCHNEIDER *et al.*, 2010; HWANG *et al.*, 2016). The focus of this work is to use formic acid (FA) as hydrogen donor.

3.4.1 Formic acid

Formic acid, CH_2O_2 or HCOOH, is a colorless liquid with pungent odor. It is the simplest member of the carboxylic acid family (ZHANG *et al.*, 2014; LIU *et al.*, 2015). Formic acid is used as a preservative, since it is an antibacterial substance. Formic acid (FA) is also used to treat pests, produce food and cosmetic additives, and to help in a variety of industrial processes (YOO *et al.*, 2014). Some of its chemical properties are listed on Table 6.

Table 6. Chemical properties of formic acid

Property	Value
Molecular weight g/mol	46,025
Flash point °C	68,89
Density g/ml	1,220
Boiling point °C	100,7
Solubility	Acetone, ethyl acetate methanol, ethanol, water
Melting point °C	8,4

The low toxicity and cost, and the high stability makes formic acid a perfect candidate to be used as internal hydrogen source (LIU *et al.*, 2015). Furthermore, formic acid can be renewably obtained in large quantities from lignocellulosic biomass (JIN *et al.*, 2008) or from electrochemical reduction of CO_2 (LEITNER, 1995), which make FA an environmentally friendly source for both high-purity hydrogen production and hydrogen donor for the CTH reaction (TEDSREE *et al.*, 2011; GONG *et al.*, 2014).

Decarboxylation/dehydrogenation of formic acid readily decomposes into carbon dioxide (CO_2) and hydrogen (H_2), under a selective catalyst. Subsequently, the hydrogen produced would be consumed on the hydrogenation of the resulting C=C bonds in the fatty acids (ROGERS & ZHENG, 2016). However, side reactions as dehydration, formation of water (H_2O) and carbon monoxide (CO), can also occur. According to RUPPERT *et al.* (2015), the reactions showed in

Figure 14 can be some of the side reactions during the decomposition of formic acid.

Figure 14. Decomposition of formic acid reactions

$$HCOOH \rightarrow H_2 + CO_2 \quad (1)$$

$$HCOOH \rightarrow H_2O + CO \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (4)$$

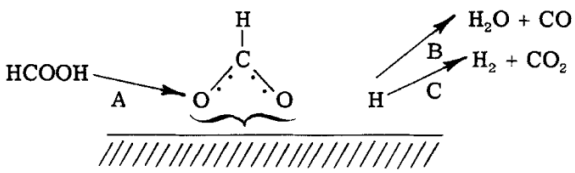
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (5)$$

$$2HCOOH \rightarrow HCHO + CO_2 + H_2O \quad (6)$$

(RUPPERT *et al.*, 2015)

Nonetheless, reactions (1) (decarboxylation), and reaction (2) (dehydration) are the most common on FA decomposition (MARS *et al.*, 1963; TRILLO *et al.*, 1972) as shown in Figure 15.

Figure 15. Formic acid reaction scheme

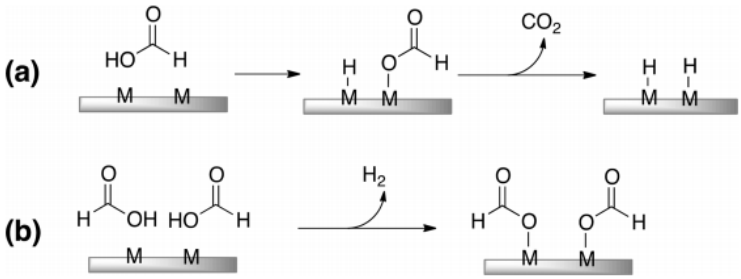


(TRILLO *et al.*, 1972)

AKIYA & SAVAGE (1998) found that water plays an important role in formic acid decomposition. The authors concluded that water acts as a homogenous catalyst on formic acid decomposition, favoring decarboxylation reaction rather than dehydration.

FUKUDA *et al.* (1968), TRILLO *et al.* (1972), IGLESIA & BOUDART (1983) and GILKEY & XU (2016) listed two surface species that directly participate in hydrogen transfer: (a) adsorbed hydrogen and (b) adsorbed formate species as represented in Figure 16.

Figure 16. Scheme proposed for hydrogen donor surface adsortion



(GILKEY & XU, 2016)

In (a) formic acid is catalytically decomposed, on the metal particles, into CO_2 and H_2. The hydrogen remains adsorbed resulting in M-H sites, where the hydrogenation of the fatty acids take place (RINALDI, 2014). In (b) when formic acid molecules collide with the catalyst surface, part is chemisorbed to form formate, and hydrogen is released (FUKUDA *et al.*, 1968).

Different catalyst, such as Pd, Pt, Ru, Rh, Raney nickel, can be used on the formic acid decomposition and hydrogen donor transfer. Supported catalyst are preferred and the most commonly employed supports are: activated carbon, alumina, silica, amorphous silica-aluminas, zeolites, $BaSO_4$, and $CaCO_3$ (KOBE *et al.*, 1991; RAJAGOPAL *et al.*, 1994). Generally, a 0,03–1,5% of the catalyst is added in relation to the starting mass of oils or fats.

KOBE *et al.* (1991), on his patent, used formic acid as hydrogen donor to hydrogenate sunflower oil (IV=139). The hydrogenation reaction takes place at atmospheric pressure in a temperature range from 20 to 90 ° C. The author, besides the hydrogen donor, also uses acetone to work as solvent. The reactor vessel contained 1 mL of oil, 0,5 mL of formic acid, 25 mL of acetone and 100 mg of 10%Pd/C catalyst were added to pursue hydrogenation. The mixture was mechanically stirred for 15 hours at room temperature and atmospheric pressure. After the reaction, the product obtained presented an iodine value of about 20, demonstrating the successfulness of the reaction.

DENG *et al.* (2010) proposed a route in which RuP/SiO_2catalyst can be used to produce g-valerolactone (GVL) from 1:1 (molar ratio) aqueous mixture of levulinic acid (LA) and formic acid. The yield achieved was 96% of GVL at 150°C.

ZHANG *et al.* (2014) research group studied the transfer hydrogenation of phenol (C_6H_5OH) on supported Pd catalyst using formic acid as an alternative hydrogen source. Palladium catalyst was loaded in different supports to test the efficacy of each one in the hydrogenation reaction. The supports studied were activated carbon (AC), MIL-101, TiO_2, Al_2O_3, and TiO_2 activated carbon composites. The performance of the catalyst with its respective support were: Pd/AC > Pd/TiO_2-AC > Pd/MIL-101 > Pd/TiO_2 > Pd/ Al_2O_3. The best

conversion yield, of 80% selectivity to cyclohexanone, was achieved with the Pd/AC catalyst under the following reaction conditions: 400 µL of formic acid with 10 mL of 0,25M aqueous phenol solution, 200 mg of Pd/AC catalyst during 4 hours. The operating conditions were mild with a temperature of 50 °C and nitrogen to purge and pressurize the system at 5 bar. The high performance of the Pd/AC catalyst was due to its specific adsorption ability for both phenol and formic acid.

GONG *et al.* (2014) studied the transfer hydrogenation of various unsaturated compounds using formic acid as hydrogen donor. The catalyst studied was Pd/CN. The reaction of the different compounds were performed as follows: 2,5 mL of water, 0,1 mmol of substrate, 0,3 mmol of FA and 10 mg of catalyst. All reactions were performed at room temperature achieving a high conversion and selectivity towards the desired product.

Another studied process using hydrogen donors is the generation of bio-jet fuel from vegetable oil by hydro-deoxygenation. Such mechanism requires a large amount of hydrogen to remove the oxygen in the molecules of oil (300-420 m^2 of H_2/ m^3 of vegetable oil). HWANG *et al.* (2016) developed a process of catalytic deoxygenation of crude Jatropha oil in assistance with hydrogen in-situ produced by formic acid solution. Conventional deoxygenation process of a triglyceride produces propane and free fatty acids in the presence of three moles of hydrogen. This study was performed in a 50 ml batch reactor using: 3 g of Jatropha oil, 3 g of formic acid solution (30%), and 0,3 g of Pd(5%)/C catalyst (previously reduced at 200 °C for 2 h with 30%H_2/N_2). The operating conditions were 300 rpm, 4h, at 340 °C. The results showed that the addition of formic acid solution as hydrogen donor is favorable for deoxygenation reaction achieving a hydrocarbon production of about 97% and deoxygenation degree of 99,5%.

GILKEY & XU (2016) collected information from different studies were formic acid acted as the hydrogen source on hydrodeoxygenation from biomass-derived feedstock. In Figure 17 is the summary of the studies, and it is possible to see that formic acid is a suitable source of internal hydrogen.

Figure 17. Hydrodeoxygenation of biomass-derived molecules with FA as hydrogen source

substrate	desired product	catalyst	solvent	temp (K)	time (h)	conversn (%)	yield (%)
HMF	DMF	Pd/C	THF + H_2SO_4	383	15	99	95
fructose	HMF	Pd/C	THF + H_2SO_4	393	1		65
fructose	HMF	Pd/C	DMSO + H_2SO_4	373	1		93
glucose	GVL	Au/ZrO_2	water + H_2SO_4	423−443	1−10	n.r.	51
fructose	GVL	Ru/C	water + tetrafluoroacetic acid	453	16	>99	52
BL	GVL	Au/ZrO_2	water	443	8	98	95
LA	GVL	$Ag-Ni/ZrO_2$	water	493	5	99	99
LA	GVL	Ru NPs	water + EtN_3	423	24	99	99
LA	GVL	Au/ZrO_2	water	423	6	>99	>99
LA	GVL	Cu/ZrO_2	water	453	2	>99	>99
LA	GVL	Pd/ZrO_2	water	423	6	n.r.	trace
LA	GVL	Cu/ZrO_2	water	473	2	100	100
glycerol	1,2-PDO	$Ni-Cu/Al_2O_3$	water	493	10	34	29
1-HB	ethylbenzene	Pd/C	water + MeOH + $FoNH_3$	353	0.5	99	98
HMF	HDL	Pd/ZrP	EtOH	413	21	97	43

[a]Abbreviations: n.r. = not reported, HMF = 5-hydroxymethylfurfural, DMF = 2,5-dimethylfuran, THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, GVL = γ-valerolactone, BL = butyl levulinate, LA = levulinic acid, 1-HB = (1-hydroxyethyl)benzene, HDL = 1,6-hexanediol.

(GILKEY & XU, 2016)

Even though the focus of the research is the use of formic acid as hydrogen donor, it is important to show a few works on different internal donors.

3.4.2 Other hydrogen donors

WOLFSON & DLUGY (2009) studies glycerol as hydrogen donor and green solvent in hydrogenation reaction. In this case, the hydrogen is transferred from the alcohol to an unsaturated bond. In the study, glycerol was used to hydrogenate different organic compounds while being dehydrogenated to dihydroxyacetone. Different homogeneous and heterogeneous catalyst were studied (Ru, Pd (5%), Raney Nickel with different supports). Reaction conditions were: 4g of glycerol, 0,2-0,55 g of substrate and the pertinent amount of metal catalyst in a 10 ml vial at 70 °C for 5-24 h. Raney Nickel's reactions showed poor conversion for the studied substrate while Pd/C catalyst showed a 80-100 % yield. Overall, the analysis of the results showed that an increase of temperature, reaction time, or catalyst loading increased the conversion in all the reactions.

MARTINELLI *et al.* (2005) researched the hydrogenation of castor oil with palladium on carbon catalyst, using limonene as solvent and hydrogen donor. The highest yield was achieved at 178 °C with 1% Pd/C and an oil/limonene ratio of 1:3 for 60 min. The percentage of hydrogenation under these conditions were approximately 67%, obtaining keto and hydroxyl stearates as main products. Another important conclusion about this work is that, at temperatures lower than 178 °C results were found not reproducible, while higher temperatures did not show any improvement in results.

ROSANA DE SOUZA SCHNEIDER *et al.* (2010) also studied limonene as hydrogen donor in the hydrogenation of sunflower oil. The reaction parameters were: 0,5-1% of Pd/C as catalyst, limonene:oil ratio of 3:1 and 2 hours of reaction. Under this conditions high selectivity for oleic acid and low concentration of stearic acid were obtained.

WANG *et al.* (2019) studied the CTH of oleic acid to octadecanol, using isopropanol as hydrogen donor. The catalyst employed was cobalt, achieving an oleic acid conversion of 100% and 91,9% of octadecanol yield at 200°C in a 4 h reaction.

Hydrolysis and hydrogenation of oil is widely studied in literature. Nonetheless, literature about one-pot hydrolysis-hydrogenation reactions are scarce. The option of carrying out both reactions in the same pot vessel represents a huge advantage, especially when an “in-situ” hydrogen donor is used. Using a hydrogen donor instead of molecular hydrogen is economically beneficent, especially when it acts as homogenous catalyst on the hydrolysis reaction at the same time. On the following chapter will be presented the methodology of the proposed procedure for stearic acid production from palm oil.

4 METHODOLOGY AND PROCEDURE

In this chapter the methodology, feedstocks, reagents, equipment and tests used during the development of this thesis will be presented. The project was carried out at Greentec (Green Technologies) laboratory at UFRJ campus in Rio de Janeiro, Brazil.

The one-pot hydrolysis-hydrogenation reaction of oil is a complex series of reactions that occur simultaneously and randomly. Nonetheless, there are three main reactions that are the focus of this study, hydrolysis and hydrogenation of the oil, and formic acid decomposition. Through scheme in Figure 18 it is possible to have a glance on the main reactions taking place for the saturated fatty acids formation.

I. Hydrolysis: The conversion of triglyceride, with the assistance of water using formic acid as homogenous catalyst, into fatty acid and glycerol. Hydrolysis occurs with the protonation of the carboxyl from the triglyceride.

II. Formic acid decomposition: With the action of the heterogeneous catalyst, the formic acid is converted into hydrogen and carbon dioxide.

III. Catalytic transfer hydrogenation: The heterogeneous catalyst assists in the reaction of the hydrogen formed with the broken double bonds of the fatty acids. Then hydrogenation takes place, converting fatty acids such as oleic into stearic acid.

Figure 18. Main reactions involved in the one-pot hydrolysis-hydrogenation of oil conversion

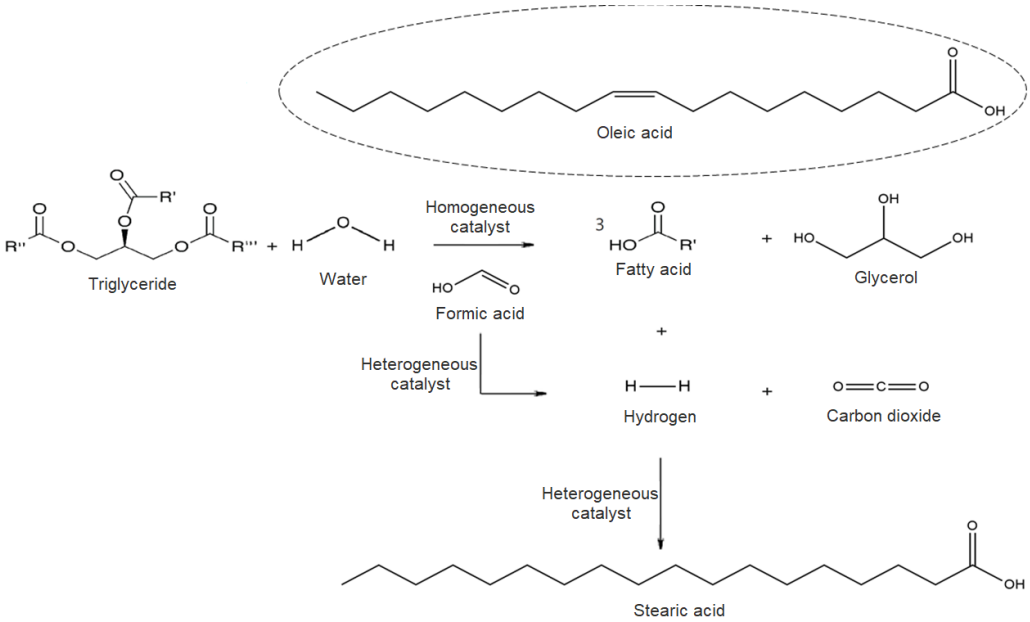
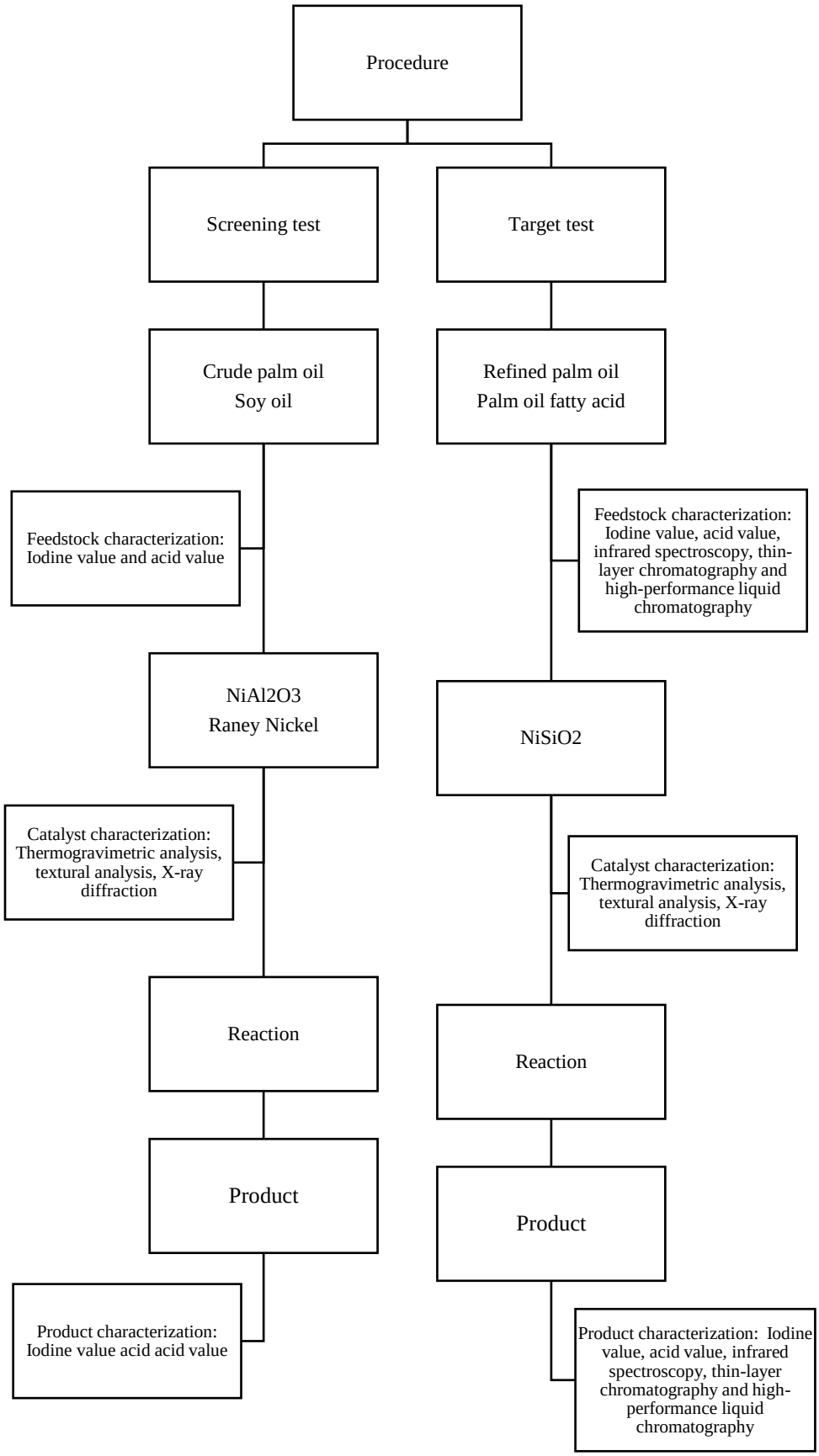


Figure 19. Project plan



Initially, the goal of the research was to produce saturated fatty acids from crude palm oil, a cheap and easily available feedstock in the northeast of Brazil, using Nickel as catalyst. Nevertheless, some challenges were presented and a few screening tests were necessary to validate some drawbacks hypothesis. This process will be further disclosed in Section 4.5. As a result of the screening tests, a slight change of the feedstock from crude palm oil to refined palm oil occurred, and an adjustment of the catalyst was necessary to achieve the goal of this research during the second set of reactions, the target tests. The plan of the project, including screening tests and target tests, is presented in Figure 19.

4.1 FEEDSTOCKS

For the screening studies, two feedstocks were used, crude palm oil and soy oil. Both oils were purchased in a local trade market, and they did not undergo any treatment before the reaction. On the other hand, refined palm oil and palm oil fatty acid were provided by Agropalma. Agroplama supplied a quality report of the feedstocks with its physicochemical characteristics as shown in Table 7.

Table 7. Quality report from Agropalma for refined palm oil and palm oil fatty acid

Property	Refined palm oil	Palm oil fatty acid
Free fatty acid (%palmitic)	0,03	76,81
Iodine value-Wijs (g I/ 100 g sample)	52,49	48,99

4.1.1 Feedstock characterization

As shown in Figure 19 the feedstocks for the screening tests were characterized with the acid value and iodine value analysis.

Feedstocks for the target tests were characterized with the acid value, iodine value, infrared spectroscopy, thin-layer chromatography and high-performance liquid chromatography analysis.

4.1.1.1 Acid value

Acid value (AV) is used to describe the amount of sodium hydroxide (NaOH) or potassium hydroxide (KOH), in milligrams, necessary to neutralize the free fatty acids in one gram of sample (SARAIVA, 2013; TUBINO & ARICETTI, 2013). %FFA (free fatty acid) is

used to describe the percentage of free fatty acids content in the oil analyzed. Such percentage needs to be analyzed in relation to an specific fatty acid such as oleic acid (MM=282 g/mol) or another fatty acid predominant in the sample (OSAWA & GONÇALVES, 2006; GARCIA *et al.*, 2014). According to the official methods Cd 3D-63 (AOCS, 2017a) and Ca 5a-40 of American Oil Chemists' Society (AOCS, 2017b) for acid value, the formula used is displayed on Equation 1.

Equation 1. Acid value and free fatty acid equation

$$AV = \frac{v * C * MM}{w}$$

v= titration volume (ml)

C = concentration of the titrant solution (mol/L)

MM= molar mass of the titrant compound (g/mol)

w = mass of the sample (g)

Knowing the AN, FFA% can be calculated with the relation expressed in Equation 2, when NaOH is the titrant solution.

Equation 2. Relation between FFA% and AN

$$FFA\% = 0{,}71\ AN$$

An adaptation of the method (Ca 5a-40) is used for the analysis of the products. The test is performed by potentiometric titration. In an Erlenmeyer of 250 ml or less, 0,2 g of sample and three drops of phenolphthalein were added as indicator. Then, 20 ml of toluene solution (1:1 v/v toluene: isopropanol) is added in the Erlenmeyer to solubilize the oil. Such solution is titrated with NaOH (0.1 M) until a permanent pink color persisted for at least 30 seconds, the color of the phenolphthalein. Standardization of the NAOH solution was performed using Potassium hydrogen phthalate ($C_8H_5KO_4$).

4.1.1.2 Iodine value

Iodine value (IV) is the measure of unsaturation of the fat since every double bond of the fatty acid can incorporate two atoms of halogen, iodine. In that order, the higher the unsaturation of a fatty acid, the higher the absorption of iodine, and therefore a higher IV.

The degree of unsaturation is important to classify oils and fats. Oils with higher IV are more unsaturated, meaning they are liquid at room temperature. On the contrary, saturated oils, with lower IV, are solid/semi-solid at room temperature (NEUZA, 2009). The result is expressed in terms of the amount of iodine (in grams) that has to be added to 100g of fat for complete saturation (ZIEVERINK, 2007).

According to standard D5768 of ASTM international (ASTM, 2003) and the AOCS Official method Tg 1a-64 (AOCS, 2009) the formula to calculate the IV is presented in Equation 3.

Equation 3. Iodine value equation

$$IV = \frac{12{,}69\ C\ (v1 - v2)}{w}$$

C = concentration of the titrant solution (mol/L)

$v1$ = titration volume of the blank (ml)

$v2$ = titration volume of the sample (ml)

w = mass of the sample (g)

The procedure to obtain the IV of an oil or fatty acid is through Wijs method by titration with Sodium thiosulphate ($Na_2S_2O_3$). The amount of sample is weighted according to the expected IV in a 500 mL glass-stoppered bottle containing 20 ml of glacial acetic acid/cyclohexane, 1:1, v/v, and pipet 25 ml of Wijs Solution into the flask. Swirl, and is let stand in the dark for 30 minutes. Then, the flask is removed and 20 ml of potassium iodide and 100 ml of distillated water are added. The titration of the excess iodine with 0.1 N sodium thiosulfate starts, adding the titrant gradually and shaking constantly until the yellow color of the solution almost disappears. Starch is added and the titration is continued until the blue color disappears entirely. Concomitantly, is always conducted a blank in the same manner and at the same temperature.

To determine the extent of the hydrogenation, ZIEVERINK (2007) defines the conversion as the fraction of the double bonds, initially present in the oil, that have been saturated and can be calculated from the iodine value with Equation 4.

Equation 4. Extent of hydrogenation

$$x = \frac{IV_0 - IV}{IV_0}$$

IV_0 = Oil's iodine value

IV = Sample's iodine value

4.1.1.3 Infrared spectroscopy

Infrared (IR) radiation is referred as the part of the electromagnetic spectrum between the visible and microwave regions. It is widely applied on the characterization of molecules. Every molecule gives a spectrum, being that any two compounds are unlikely to give exactly the same IR spectrum (SILVERSTEIN *et al.*, 2014). Such spectrum is represented as the absorbance or transmittance vs. the frequency or wavelength, which will depend on the relative masses of the atoms, the force of the bonds, and the geometry of the atoms. The spectrum helps to identify the composition of a sample.

The device used for the test was the Shimadzu IRPrestige-21. The spectrums were obtained from 400 to 4000 cm^{-1} in absorbance with resolution of 1 cm^{-1} with 64 scans per spectrum.

4.1.1.4 Thin-layer chromatography

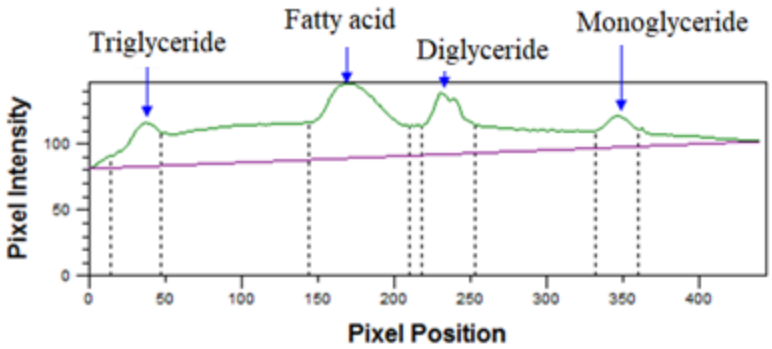
Thin-layer Chromatography (TLC) is the simplest chromatographic methods. It is essentially use on qualitative and semi quantitative analysis (SHERMA & FRIED, 2003). The procedure is as follows: It is weighted 0,01 g of the sample and then dissolved in 1 mL of chloroform. Then an aliquot of 0,3 µL is applied in a silica gel plate 60 TLC (Merck) of size 10 X10 cm with the help of a 10 µl automatic pipette. Next, it is placed into the mobile phase composed by a mixture of petroleum ether / diethyl ether / acetic acid (70: 30: 2) (v / v) inside a closed chamber. The components of the mixture migrate during the movement of the mobile phase through the stationary phase. After the elution the chromatographic plate was revealed by dying the zones in a saturated chamber with iodine vapor, the retention factor (Rf) of the feedstocks and components of the samples was determined. To achieve irreversible staining the TLC plate was maintained in a solution of 0,63 g of $MnCl_2$ $4H_2O$, 60 mL of water, 60 mL of methanol and 4 mL of sulfuric acid for 10 seconds, followed by heating at 105 °C. The intensity of the staining depends on the heating time, which should be no less than 30 min.

After completing this procedure, a photo of the plate was taken and with the help of the program Image Master Total Lab version 1.11 that quantified the areas of the compounds. The

main purpose of this test was to identify qualitatively and semi-quantitatively the composition of the products identifying the unsaturated compounds.

In Figure 20 is a representation of the bands obtained from the program. Every stain in the plate represents a different compound and depending on the position of the stain (Rf) and its intensity, a peak is formed in the chromatogram. The more nonpolar the component, the higher the Rf, since its interaction with the stationary phase is lower. As can be seen on the figure every peak is assigned to a compound. The first peak represents the triglyceride, the second the fatty acid, the third the diglyceride and the fourth the monoglyceride presence. The program calculates the area of every peak. Such area can be used to have an estimation of the percentage on the composition of the sample of the unsaturated compounds.

Figure 20. Compounds identification bands on TLC



4.1.1.5 Gas Chromatography with Flame-Ionization Detection

Gas Chromatography with Flame-Ionization Detection (GC-FIC) was employed to validate the conversion of unsaturated fatty acids on saturated ones. To carry out this analysis the fats must be converted to esters. Direct GC analysis of fats is difficult because of the high boiling points of tri-glycerides and fatty acids (ZIEVERINK, 2007). Hence, a transformation through methanolysis of the product's fatty acids on fatty acid methyl esters (FAME) was necessary. The procedure followed was an adaptation of KYRIAKIDIS & DIONYSOPOULOS (1983) and YOO *et al.* (2010). For the methanolysis, five grams of sample were mixed with 20 mL of methanol solution (10% HCl). Then placed in a closed and sealed tube at 75 °C bain-marie for an hour.

The product of the reaction was cooled down, and 10 mL of distilled water with 10 mL of hexane were added to separate the aqueous and organic phase. The upper phase containing the FAME dissolved in hexane was heated to evaporate the solvent and recover the desired

product. Subsequently, the FAME is diluted with heptane in a proportion of 0,05:1 in volume, injecting one microliter of sample on the chromatographer.

The chromatography analysis was carried out using an adaptation of the EN14103 method in a Shimadzu gas chromatographer GC-FID/2014 model, with split ratio of 1:30, flame ionization detector (FID), Carbowax column (30m x 0,32mm x 0,25µm) from Quadrex, under the following chromatographic conditions: injector temperature of 250°C, detector temperature of 250 ºC, hydrogen as carrier gas (99,999%) with a flowrate of 2,14 mL/min. The program started at 60 °C for 2 min, then heats up up to 200 °C at 10 °/min, then 200 °C to 250 °C at 15 °C/min, stays in that temperature for 10 minutes. Overall analysis duration was 29,33 min.

4.2 REAGENTS

All reagents used were analytical grade. Distillated water was used in all measurements and reactions. The fatty acids sample (FAME mix) was from Sigma Aldrich.

Nitrogen used to pressurize the system, and also to suppress oxidation by removing atmospheric oxygen, gas purchased from Air Products with a purity of 99,9992 %. In some reactions, hydrogen was used with specific purposes beyond pressurizing the system, as will be further explain. Hydrogen was bought from Air Products with a purity of 99,9992 %.

4.3 HOMOGENEOUS CATALYST

Formic acid works as a homogenous catalyst for the hydrolysis reaction. The acid was purchased from Sigma Aldrich with a purity of 98-100%.

Apart from performing as a catalyst, plays an essential role as hydrogen donor for the hydrogenation reaction. Formic acid is the perfect candidate to be hydrogen donor agent due its low toxicity, cost, and high stability (LIU *et al.*, 2015). Furthermore, formic acid can be obtained in large quantities via hydrogenation of waster carbon dioxide from industry, biomass processing and artificial photosynthesis, which make it easily available and affordable (GONG *et al.*, 2014).

4.4 HETEROGENEOUS CATALYST

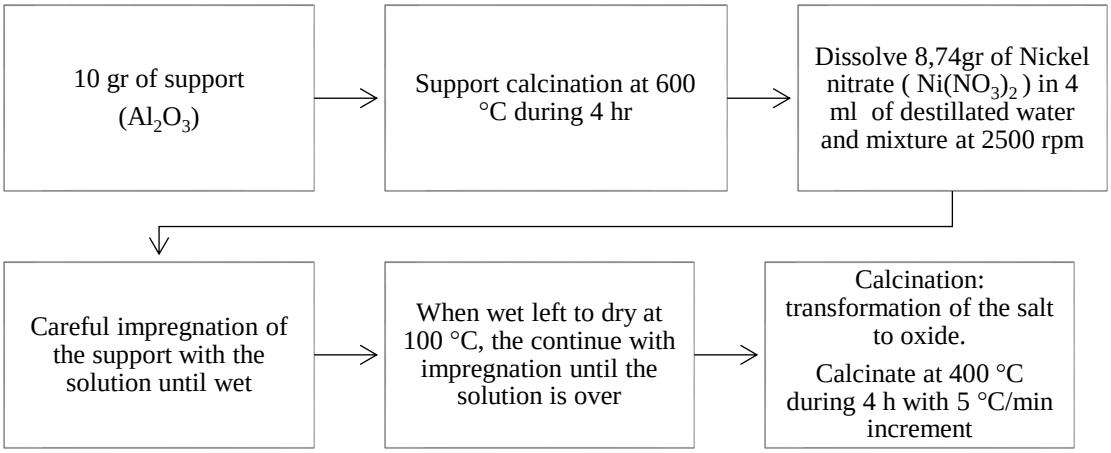
The use and application of metal catalyst on hydrogenation reactions has been widely studied and documented (JAN, 1979; CHENG *et al.*, 2012; LIST & KING, 2016). Noble metals have great selectivity and high catalytic activity, although they are expensive. On the other hand, Nickel, a transition metal, is perfect candidate considering its low cost, wide availability and good performance on the desired reaction. For the screening tests the performance of Nickel-Aluminum ($NiAl_2O_3$) catalyst and the commercial Raney Nickel were studied. For the target tests, active Nickel supported Silica ($NiSO_2$) catalyst was employed.

4.4.1 Heterogeneous $NiAl_2O_3$ catalyst preparation

The method used for the preparation of the heterogeneous catalyst was incipient wetness impregnation (IWI) (MUNNIK *et al.*, 2015). First, 8,74 gr of the active metal precursor, Nickel nitrate ($Ni(NO_3)_2$), is dissolved in 4 ml of distillated water to form an aqueous solution. Such solution is added carefully to 10 gr of the previously calcined solid catalyst support, (Al_2O_3). Then the support is carefully impregnated until wet. When the supports gets too wet, it is dried out in a furnace. This process is repeated until the aqueous solution is completely incorporated in the support (DERAZ, 2018). Afterwards, the impregnated support was calcined to drive off the volatile components within the solution, depositing the metal in the catalyst surface. The Nickel catalyst synthetized supported in Alumina was prepared with a Nickel loading of 15%.

Subsequently, the calcination process was carried out at 400°C during four hours (BARTHOLOMEW & FARRAUTO, 1976). The procedure followed for the synthesis of the catalysts is showed in Figure 21.

Figure 21. Procedure for catalyst synthesis



4.4.2 Commercial catalyst

Raney nickel (RN) catalyst was provided by PROCAT with a content of 50% of metal. Active Nickel Silica (NiSi) supported catalyst (PRICAT 9932) with a content of 22 wt% nickel was provided by Johnson Matthey catalysts. Both catalyst are in pellets form, where the active nickel is covered with hardened vegetable fat as protective structure.

The reason why catalyst PRICAT 9932 was selected is because of its especially high resistance to nickel soap formation (LIST & KING, 2016). This catalyst is also used when hydrogenation conditions requires mild pressure and moderate low temperatures.

4.4.3 Catalyst characterization

Some catalyst characterization techniques were used in order to understand how the catalytic performance of the reaction was related to the catalyst properties.

Textural analysis was carried out at *GreenTec* laboratory. X-ray diffraction and Thermogravimetric analysis at *LabTech* laboratory. Both laboratories from *Escola de Quimica* at UFRJ University.

4.4.3.1 Thermogravimetric analysis (TGA)

TGA measures the weight change amount of a material, as function of increasing temperature or time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. It is

performed with a thermogravimetric analyzer or thermobalance (GROENEWOUD, 2001). The objective is to illustrate the thermal stability of the catalyst. The result gives information about physical phenomena, such as phase transition, absorption and desorption: as well as chemical phenomena as chemisorption, thermal decomposition, oxidation and/or combustion (HERMIDA *et al.*, 2018).

A more illustrative representation of the degradation is through differential thermogravimetric ratio (DTG), which is the representation of the first derivative of TGA. The peak height at any temperature gives the rate of mass loss.

The instrument used for the analysis was the TA/SDT Q600 device. The analysis was performed using a weight sample from 8 to 11 mg on nitrogen flow (100 mL/min). The temperature ramp was 10 °C/min up to 800 °C for the Nickel alumina (NiAl) catalyst and 1000 °C for the commercial catalysts.

4.4.3.2 Textural analysis

Textural properties of catalyst are aimed to determine the physical characteristics of the catalyst sample, such as surface area, pore volume and pore diameter, among others. This measurement is important to determine the surface area or, in other words, the reactive surface available to interact with the reactant medium. A way to determine such properties is by the relation of gas volume absorbed by the porous structures, in function to the relative pressure of the gas using different mathematical models (FAGERLUND, 1973).

The measurement of those properties were carried out using nitrogen adsorption-desorption isotherms employing the BET (Brunauer, Emmet and Teller) method for the surface area, and BJH (Barret, Joyner and Halenda) method for pore distribution (BRUNAUER *et al.*, 1938; BARRETT *et al.*, 1951). The instrument used was the Micrometitics ASAP 2020. With the information obtained from the TGA the commercial catalyst is thermally treated before the analysis to remove the fatty protective layer in order to avoid problems with the equipment. Later, 0,3 g of the sample was weighted. Then, it was pre-treated in inert atmosphere and vacuum to remove traces of water or volatiles at 300 °C overnight. After the pre-treatment the sample is weighted again to determine the real weight and the analysis is started.

4.4.3.3 X-ray diffraction (XRD)

XRD provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects (ANDREI A. BUNACIU *et al.*, 2015). The X-ray diffraction technique is a plot of the intensity of X-rays distributed at different angles by a sample. The XRD pattern is like a fingerprint that helps to figure out the composition of the catalyst and also to determine the crystallinity and a phase of a compound. The instrument used was the Rigaku Miniflex II with a diffractometer with graphite monochromator. The diffraction patterns were recorded by varying 2θ from 5° to 90° at scanning speed of 0,5° per second. Thermic pretreatment for the commercial catalyst was performed before carrying out the XRD test, to avoid interference of the coating in the analysis.

From the difractogram there is another information that can also be obtained, the medium size of the particles. The formula use is the Scherrer equation that is written as presented on Equation 5.

Equation 5. Scherrer equation for medium size particle calculation

$$d = \frac{k\lambda}{\beta\cos(\phi)}$$

d= mean size of the particles

k= dimensionless shape factor

λ= X-ray wavelength

β=is the line broadening at half the maximum intensity (FWHM)

ϕ= Bragg angle

4.5 EXPERIMENTAL PLANNING

The reactions were carried out in a batch Parr high pressure reactor (Parr 4848 Reactor Controller) equipped with an external electrical furnace and stirrer, as presented in Figure 22. The reactor is made of stainless steel, has a capacity of 100 mL and can withstand an estimated maximum pressure of 200 bar. The temperature in the reactor was measured by a thermocouple and controlled at the set temperature.

Figure 22. 4848 Parr reactor

Although no formal experimental design was carried out, the planning was divided in two segments, as stated at the beginning of this chapter, the screening and target tests. Such tests were executed in a way that was possible to understand the behavior of the reaction under different conditions.

The variables and constants were selected based in the literature as well as hydrolysis and hydrogenation. Some of the main references were, ALBRIGHT (1963), ANNEKEN *et al.* (2012), DIAZ (2012), LIST & KING (2016). The constants set for all experiment were as temperature (190 °C) and heterogeneous catalyst loading (3 wt% with reference to weight of oil) and 40% of headspace. The constants were defined based on the results of previous works of the research laboratory were the project was developed.

Stoichiometrically the water:oil molar ratio is 3:1 (3 moles of water per 1 mole of triglyceride). For formic acid, since approximately 50% of the fatty acids are unsaturated and assuming that such 50% has double unsaturation, a 3:1 molar ratio (3 moles of formic acid per 1 mole of triglyceride) is required to form the moles of hydrogen necessary to hydrogenate the double bonds. Just a 1:1 FA:oil molar ratio, is necessary to carry out the hydrolysis of the oil (FREEDMAN *et al.*, 1984; WANG *et al.*, 2006).

4.5.1 Screening tests

A set of initial tests were performed to evaluate the success of the reaction when using crude palm oil as feedstock, and NiAl and RN as catalyst as presented on Table 8. The time length of reaction for this set of experiments was eight hours under the following parameters:

agitation 600 rpm (DIAZ, 2012), nitrogen pressure of 14 bar (ALBRIGHT, 1963) and molar FA:oil ratio of 6:1, which is an excess of the minimum amount of formic acid required to carry out the reaction. The agitation rate and nitrogen pressure were defined by experimental conditions. Two levels of water were tested, one following the stoichiometry of the hydrolysis reaction and the other with excess of water, since there is no limitation reported in the literature.

Table 8. Reaction tests with crude palm oil

Test*	Catalyst type	molar ratio water: oil
SP1	None	15:1
SP2	RN	15:1
SP3	NiAl	15:1
SP4	NiAl	3:1

* Reaction parameters: molar formic acid:oil ratio of 6:1. Agitation 600 rpm. 8 hours of reaction. 14 bar of Nitrogen pressure.

Soy oil was tested in a shorter reaction time (three hours). Same reaction parameters as before were used in this set of tests. However, molar FA:oil ratio was varied based on KOBE *et al.* (1991), to determine whether its increment improves the hydrogenation extent. Additionally, one more level of water was tested as shown on Table 9.

Table 9. Reaction tests with soy oil

Test*	Catalyst type	molar ratio water: oil	molar ratio FA: oil
SS1	None	3:1	12:1
SS2	None	10:1	12:1
SS3**	NiAl	3:1	0
SS4	RN	10:1	12:1
SS5	RN	15:1	6:1
SS6	RN	15:1	6:1

* Reaction parameters: Agitation 600 rpm. 3 hours of reaction. 14 bar of nitrogen pressure

**Hydrogen instead of nitrogen

A reevaluation of the parameters based in the literature and in the results of this screening tests was performed and implemented for the upcoming tests. Nitrogen pressure and agitation rate were also defined by experimental conditions.

4.5.2 Target tests

Twelve target tests were carried out under the following conditions: 190°C, 750 rpm (ALBRIGHT, 1963; DE OLIVEIRA LIMA *et al.*, 2007), 20 bar of initial pressure (ANNEKEN *et al.*, 2012), 4 hours of reaction, 40% of headspace, and 3 wt% of heterogeneous catalyst loading. The water level selected for this tests was 5 molar ratio water:oil which represents an small excess of the stoichiometric relation.

As for formic acid two levels were tested. One in relation to the stoichiometric ratio and the other based on KOBE *et al.* (1991), which corresponds to 1:1 volume relation of formic acid to oil (25 molar ratio). Table 10 shows the summary of the reactions performed.

Table 10. Reaction test with refined palm oil

Reaction type	Test*	Feedstock	Catalyst	Reaction time (h)	Gas type	molar ratio water: oil	molar ratio FA: oil
Hydrolysis kinetic curve w/o heterogeneous catalyst	1	RPM	None	4	N_2	5:1	0
	2	RPM	None	4	N_2	5:1	3:1
	3	RPM	None	4	N_2	5:1	25:1
Hydrogenation w/o formic acid	4	RPM	NiSi	4	H_2	0	0
	5	RPM	NiSi	4	H_2	5:1	0
Influence of formic acid in hydrogenation	6	RPM	NiSi	4	N_2	5:1	3:1
	7	RPM	NiSi	4	N_2	5:1	25:1
Reaction time one-pot reaction	8	RPM	NiSi	10	N_2	5:1	3:1
	9	RPM	NiSi	48	N_2	5:1	3:1
Fatty acid hydrogenation	10	POFA	NiSi	4	N_2	0	3:1
	11	POFA	NiSi	4	H_2	0	3:1
	12	POFA	NiSi	4	H_2	5:1	3:1

* Reaction parameters: Agitation 750 rpm. 20 bar of nitrogen pressure

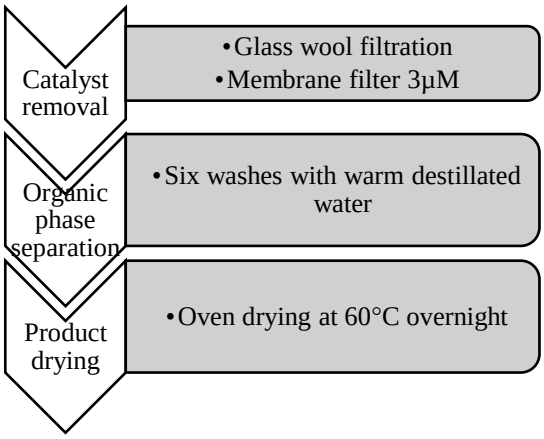
4.6 ONE-POT HYDROLYSIS-HYDROGENATION REACTION

The steps followed to carry out the reactions were the same for all set of tests. The amount of every reactant was calculated using the goal seek function in a Microsoft Excel spreadsheet, to achieve the 40% headspace determined (60 mL) based on the ratio of the reactants related to the oil. Once the measure of the feedstock, reactant and catalyst are calculated they are weighed to pursue the reaction. First, if the catalyst to be used is NiAl, a previous reduction the day before the reaction is necessary. Such reduction was performed in a tubular furnace at 400 °C during 4 hours with an increment on temperature of 5 °C/min, using as reductant agent hydrogen with a purity of 99,9992 % and flow rate of 50 mL/min

(BROECKER *et al.*, 1975). For the commercial catalysts, such reduction was not needed since the Nickel in the pellet is active. Then, the oil is placed in the reactor vessel followed by the catalyst, formic acid and water, when required. Next, the vessel is closed, purged and pressurized using nitrogen. The reaction is programmed at 190 °C at the corresponding agitation rate. The heater is turned on and the reaction time is started once the set temperature is reached (approximately in one hour). At the end of the reaction, the final pressure is registered, the heater turned off and the reactor is cooled down (approximately in one hour). Since the expected product is semi-solid at room temperature, the reactor is open at 70 °C, while the mixture is still in liquid phase to start the treatment of the product.

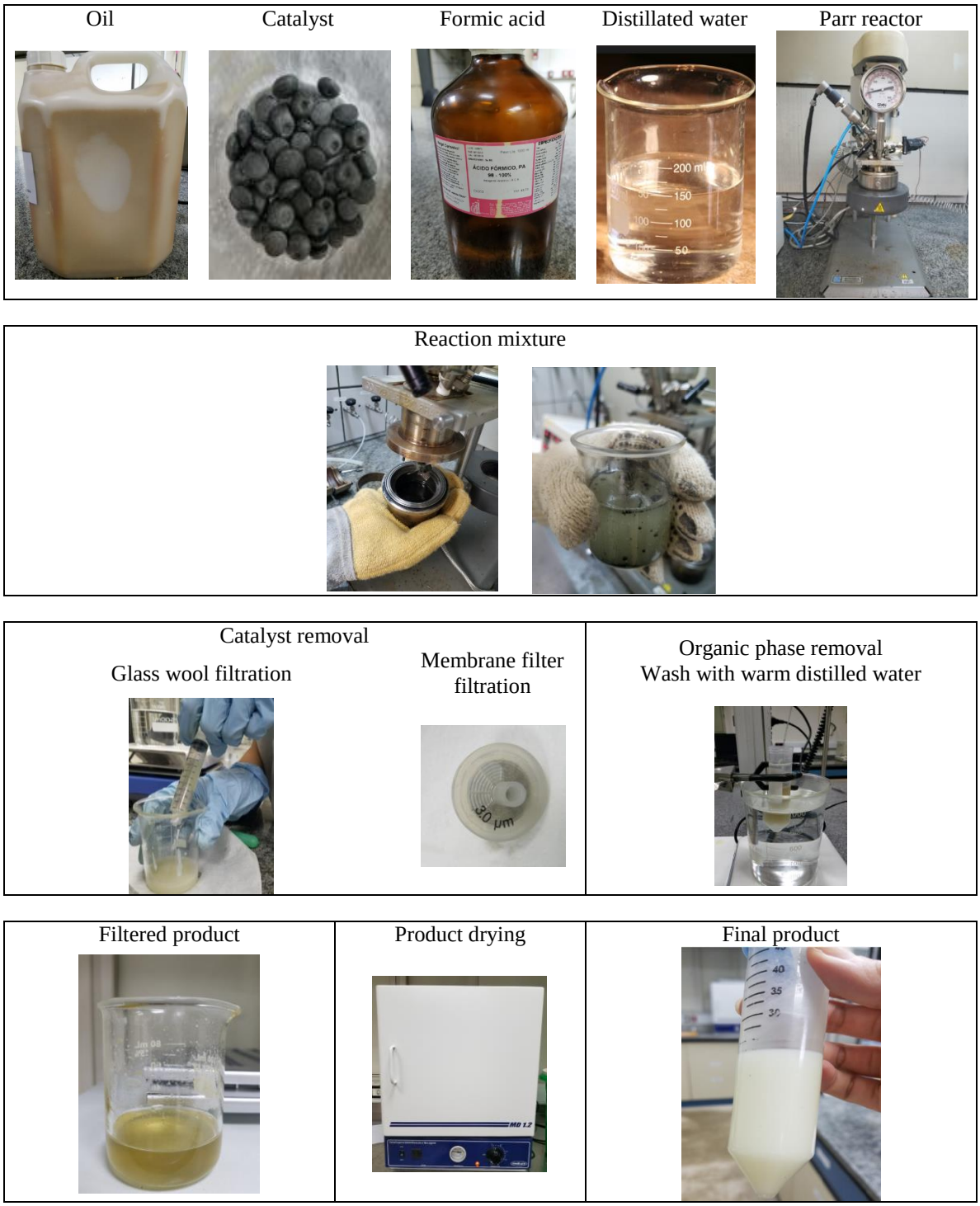
Because of the complex nature of the reaction product, containing a mixture of catalyst, saturated and unsaturated triglyceride, fatty acids, water, glycerin and probably formic acid, a process for treating the product, with the aim to obtain fatty acids as pure as possible, was perform as shown in Figure 23.

Figure 23. Scheme of product treatment



Throughout the process, the product is in a falcon tube submerge at bain-marie to keep the mixture liquid. From Figure 18, the first step is the removal of the catalyst. Considering the particle size of the catalyst and the consistency of the product a double filtration process was necessary. The first one uses a glass wool to remove most amount of catalyst as possible. The second one is needed to remove any traces of catalyst using a micro membrane filter (3µm, PP/PTFE). Afterwards, the filtrated mixture is washed with warm distillated water to separate the aqueous phase (glycerol, water, formic acid) from the organic phase containing the product of interest. The organic phase is placed in a beaker and dried in an oven overnight at 60 °C to remove any remains of humidity for further storage and analysis. In Figure 24 is the graphic representation of the steps mentioned before.

Figure 24. Graphic representation of the procudure of the one-pot hydrolysis-hydrogenation of palm oil



4.6.1 Product characterization

As shown in Figure 19 the products for the screening tests were characterized with the acid value and iodine value, two quantitative test.

On the other hand the products for the target tests were characterized, besides acid value and iodine value, the monitoring product analysis, with other analysis with the purpose of supporting the results of the quantitative methods, and have a better identification of the main composition of the product sample. Infrared spectroscopy, thin-layer chromatography and high-performance liquid chromatography.

4.6.1.1 Monitoring product analysis

- Acid value: An adaptation of the method (Ca 5a-40) is used for the analysis of the samples as described on Section 4.1.1.1.

- Iodine value: The procedure to obtain the IV of an oil or fatty acid is through Wijs method by titration with Sodium thiosulphate ($Na_2S_2O_3$), following the AOCS Official method Tg 1a-64 as described on Section 4.1.1.2.

4.6.1.2 Additional product analysis

- Infrared spectroscopy: Infrared spectroscopy was performed in the device Shimadzu IRPrestige-21 as described on Section 4.1.1.3.

- Thin-layer chromatography: Thin-layer Chromatography was carried out as described on Section 4.1.1.4.

- Gas Chromatography with Flame-Ionization Detection: Gas chromatography analysis was carried out using an adaptation of the EN14103 method in a Shimadzu gas chromatographer GC-FID/2014 model, as described on Section 4.1.1.5.

5 RESULTS AND DISCUSSION

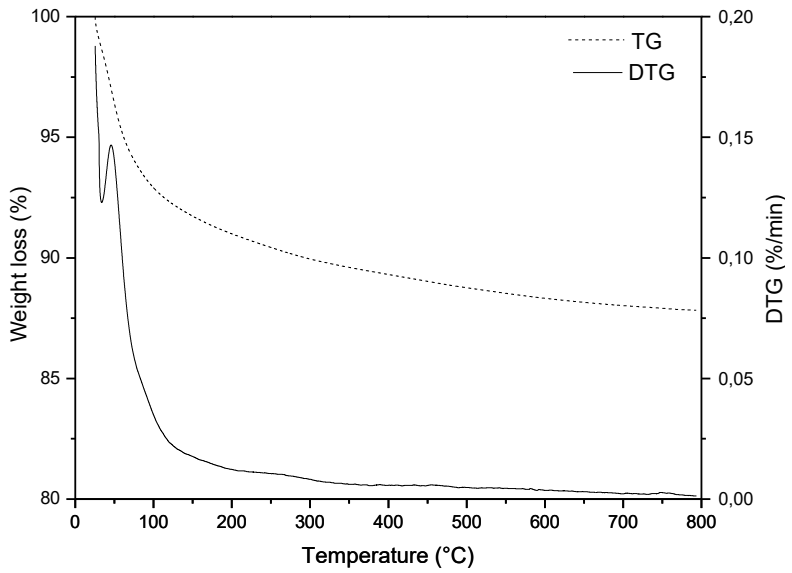
This chapter will present and discuss the results of the catalyst characterization, the analysis from the feedstocks, and the products from the screening and target tests.

5.1 CATALYST CHARACTERIZATION

5.1.1 Thermogravimetric analysis (TGA)

The thermogravimetric profile of Nickel Alumina catalyst was analyzed under a temperature up to 800 °C, as shown in Figure 25.

Figure 25. TGA and DTG curves for Ni/Al_2O_3 catalyst

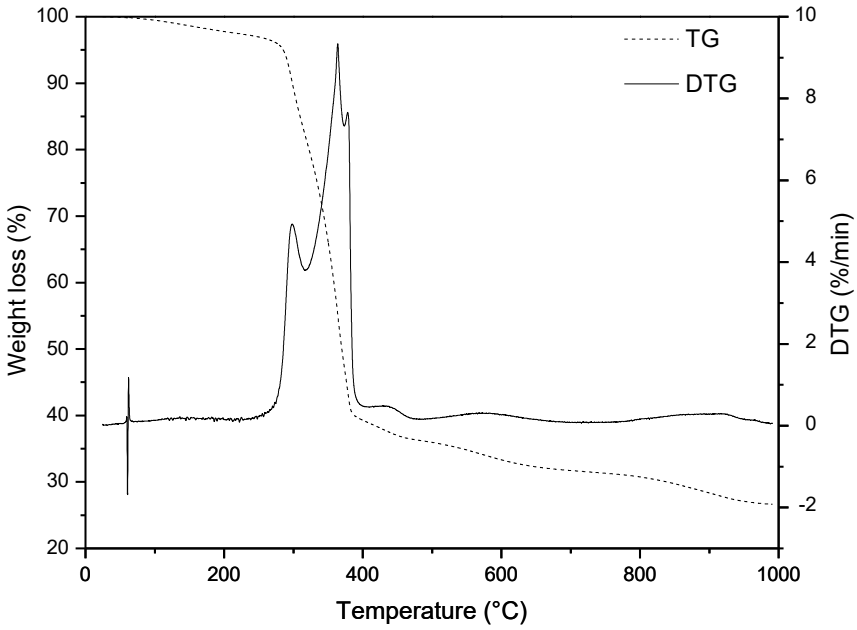


Peaks below 300°C represent the elimination of the physisorbed and chemisorbed water (BARTHOLOMEW & FARRAUTO, 1976; TAGLIAFERRO *et al.*, 2005; DUBEY & KAURAV, 2017; HERMIDA *et al.*, 2018).

For NiAl catalyst, the TGA analysis is important to understand its stability during the calcination process at 400 °C. From Figure 25 it can be seen a weight loss of nearly 2% in the temperature range of 25-46 °C, and 7,5% at 46-350°C. After 350°C no further thermic degradation occurs. Both peaks could mean water and volatiles impurities elimination, with different bonding to the catalyst structure, representing 9,5% of the total catalyst mass.

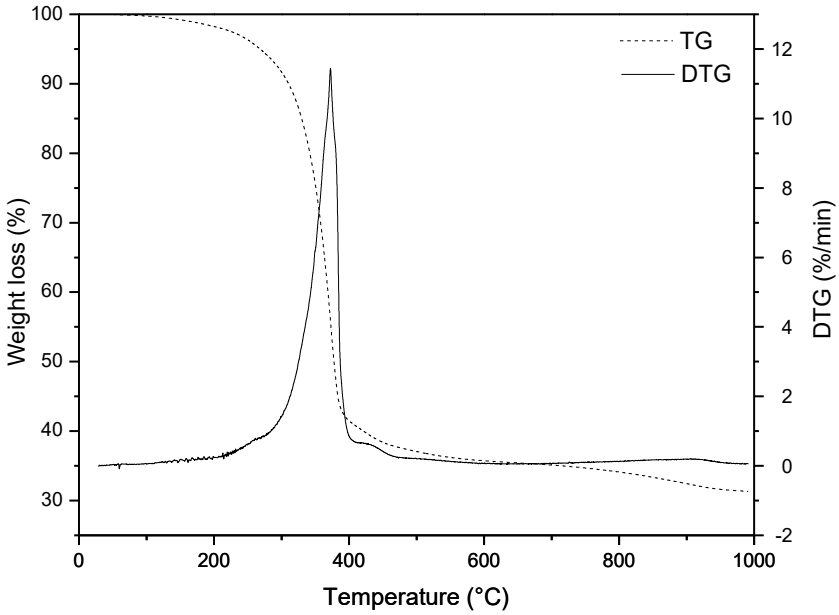
Even though commercial catalysts did not undergo any thermal process before its use, it is relevant to illustrate its thermogravimetric behavior. Raney Nickel and Nickel Silica were tested up to 1000 °C as shown in Figure 26 and Figure 27, respectively. Peaks at temperatures above 300°C could symbolize the evaporation of the hardened fat present on the commercial catalyst.

Figure 26. TGA and DTG curves for Raney Nickel catalyst



In Figure 26, Raney Nickel catalyst shows different peaks at different temperature ranges. This is explained because commercial catalyst, in order to preserve the active metal, uses different compounds to work as coating and passive to prevent the oxidation of the metal. At the end of the test, at 1000 °C, the weight loss was approximately 72,2%. According to RASE (2016), a typical catalyst with a protective layer has hardened oil content of about 50-77%. Therefore, a weight loss of 72,2% is normal for this kind of pellet catalyst. Likewise, the NiSi catalyst in Figure 27 presents a sharp peak between 273 and 413 °C on the DTG curve. This peak corresponds to nearly 59,4% of weight loss.

Figure 27. TGA and DTG curves for Ni/SiO_2 catalyst



5.1.2 Textural analysis

The data of the analysis containing the surface area, pore volume and diameter of different catalyst are presented in Table 11.

Table 11. Textural analysis of the catalysts

Catalyst	Surface area (m^2/g)	Pore diameter (Å)
$NiAl_2O_3$	153	90,96
Raney Nickel	224	46,31
$NiSiO_2$	229	40,44

For the textural analysis, the commercial catalyst was powdered and thermally treated to drive off the fat protective layer.

Surface area has a big influence on the material absorption capability, the higher the surface area, the higher the extent of active sites and the higher adsorption capability. According to LOK *et al.* (1984) the desired surface area for a $NiAl_2O_3$ is between 100-250 m^2/g and a pore diameter of 10-50 Å. RASE (2016) expresses that nickel catalyst for hydrogenation need a surface area of 200-600 m^2/g and a pore diameter of 50-110 Å.

NiAl catalyst shows the lowest surface area but the higher pore diameter out of the three catalyst tested. With a higher pore diameter, the molecules access to the internal active sites is much easier. The difference between the parameters of the textural analysis are relatively low

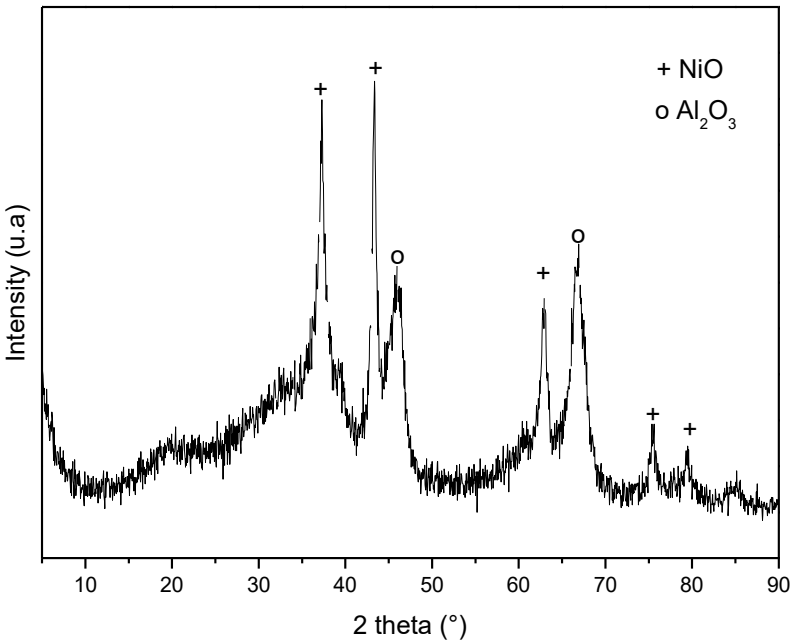
for the commercial catalyst, both within the range of the expected surface area and pore diameter. Nonetheless, a higher surface area and pore diameter would be preferred.

5.1.3 X-ray diffraction (XRD)

The catalyst diffractograms are presented in Figure 28 for Nickel Alumina, and in Figure 29 and Figure 30 for the commercial catalyst, Raney Nickel and Nickel Silica respectively. As stated on the methodology section, in order to pursue the XRD test effectively, it was necessary a thermic pretreatment of the commercial catalyst pellets to drive off the fat and prevent its interference on the test.

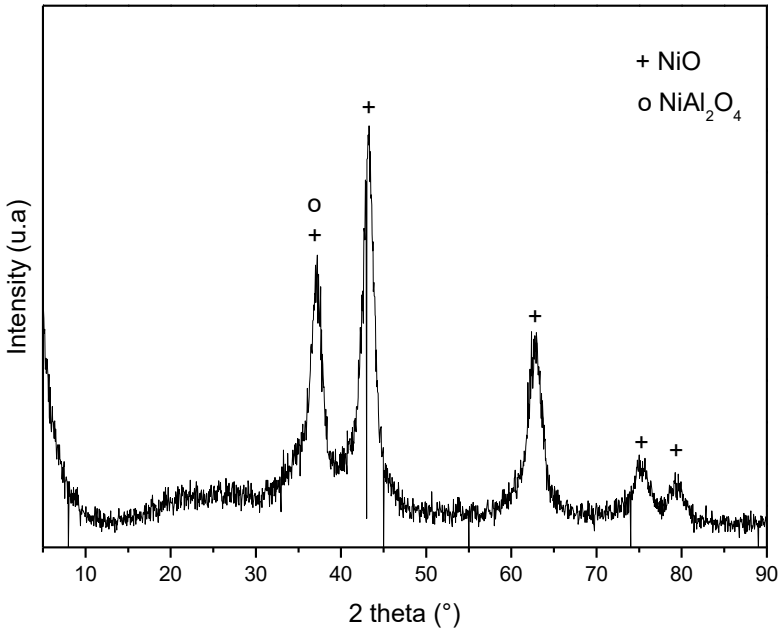
The crystalline phases were identified by comparison with JCPDS standards (THYSSEN *et al.*, 2015; LEE *et al.*, 2017). The peaks appearing at 2θ = 46,1° and 66,5° were attributed to the support structure of Al_2O_3 (JCPDS 82-1468). Signals related to NiO were identified at 2θ = 37,3°, 43,3°, 63,3°, 75,5° and 79,5° (JCPDS 47-1049).

Figure 28. X-ray diffraction of Ni/Al_2O_3 catalyst



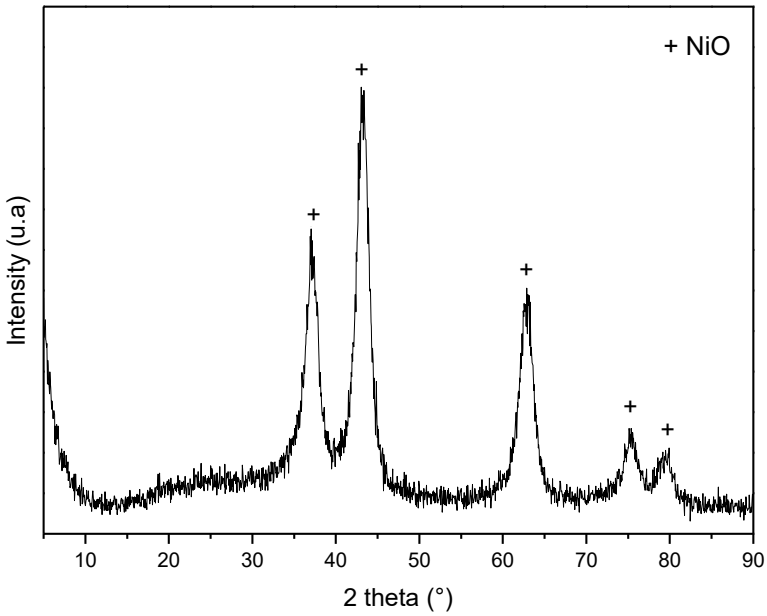
Furthermore, for the Ni Raney catalyst was identified a signal corresponding to $NiAl_2O_4$ (JCPDS 10-0339) at 2θ = 37,2° overlapping a signal related to NiO.

Figure 29. X-ray diffraction of Raney Nickel catalyst



The Nickel Silica catalyst diffractogram do not show additional peaks other than Nickel Oxide, the reason is because the support of the catalyst could be amorphous (LARIBI *et al.*, 2012).

Figure 30. X-ray diffraction of Ni/SiO_2 catalyst



It is important to highlight that Nickel is in its metallic form and not as an oxide. However, because of the thermal process to remove the fat layer of protection, Nickel became exposed to air and oxidize after the thermal treatment.

From the Scherrer equation (Equation 5), the average particle size was calculated for all three catalyst based on their XRD, shown on Table 12. It was found that the synthesized NiAl catalyst had the lower particle size, meaning that such catalyst has a bigger exposed area. Therefore, more advantage of the metal can be taken.

Table 12. Particle size from Scherrer equation

Catalyst	Crystallite size (nm)
NiAl	0,045
NiSi	0,088

5.2 FEEDSTOCK AND PRODUCT CHARACTERIZATION

5.2.1 Screening tests

As said before, the initial tests were performed using crude palm oil as feedstock, on Table 13 some physicochemical properties used to evaluate the conversion of the oil are presented. To monitor the hydrolysis and hydrogenation progress, the acid value and iodine value were implemented. Those two analytical tests are standard to classify and evaluate oils and fatty acids commercially. To express how much of the sample was hydrogenated in relation to the initial oil, the extent of hydrogenation on Equation 4 was used. Additionally, to have an idea of the maximum acid value to be obtained, the product specification of a commercial stearic acid (~57% C16 and ~42% C18), by THECHEMICALCOMPANY (2019), has an acid value of 146-150 mg NaOH/ g sample. The result those analysis is showed on Table 14.

Table 13. Physicochemical properties of crude palm oil

Properties	Crude palm oil
Acid value (mg NaOH/g)	0,426
Iodine value (g I/100 g)	64

Three reactions were performed to evaluate the performance without catalyst and with the two catalysts selected (SP1, SP2 and SP3), with a molar water:oil ratio of 15:1. SP1 is the blank test without heterogeneous catalyst. The expected result was a high conversion on free fatty acids and low saturation, such expectative is consistent with the result obtained. However, with the addition of heterogeneous catalyst (NiAl and RN) for the following test, it was expected an increment of the conversion to saturated fatty acid, represented by IV. Nonetheless,

for all performed tests, the conversion continued practically unaltered. As stated before, Nickel alumina and Raney nickel are well known catalyst for use on hydrogenation processes, but still there was no notable conversion.

On SP4 a different level of water was tested. When comparing SP3 and SP4 it can be concluded that a big excess of water is not necessary in order to achieve high hydrolysis conversion.

Table 14. Reaction tests with crude palm oil produt analysis

Test	**Catalyst type**	**AI (mg NaOH/g sample)**	**IV (gr I/100g sample)**	**Extent of hydrogenation (%)**
SP1	None	128	62	3
SP2	RN	113	62	3
SP3	NiAl	118	62	3
SP4	NiAl	119	62	3

From this test, a higher hydrolysis conversion was obtained. Unfortunately, the extent of hydrogenation was insignificant. To explain the unsuccessful hydrogenation there are two known drawbacks in the literature.

The first one is: feedstock impurity. If the feedstock is not completely refined can contain free fatty acids, soaps, phospholipids, sulphur compounds, pigments, water or moisture, and other accompanying compounds that can affect the catalyst (SCHMIDT, 2000). Furthermore, crude palm oil contains a significant amount of beta-carotenes (500-2000 ppm) (MACLELLAN, 1983; GIBON *et al.*, 2007). Beta-carotene is from the carotenoid family and its basic structure are isoprene units, with a conjugated chain (MERHAN, 2017). The conjugated chains are the responsible for the reddish color of the oil. So, both unsaturation from the beta-carotenes and the fatty acids can compete for consuming the hydrogen available. An indication that the beta-carotenes are consuming the hydrogen is the change on the color, from dark red to a lighter one. It would indicate that the conjugated chains (characteristics of the red color) are being hydrogenated. In Figure 31 is exemplified the oil before and after the reaction, and it can be seen how the color got lighter, meaning that a hydrogenation of the beta-carotenes occurred.

Figure 31. Oil before and after the reaction

Before the reaction

After the reaction

Therefore, it can be deduced that the hydrogen formed, from the formic acid, was not enough to carry out both hydrogenations, therefore affecting the extent of reaction related to hydrogenation of the fatty acids. For such reason, it is recommended to use refined oils to pursue hydrogenation reactions and avoid secondary reactions that can take the hydrogen available (ALBRIGHT, 1963; HASTERT, 1979).

The second drawback is: nickel soap formation or nickel saponification (DROZDOWSKI & ZAJAC, 1977; BARTHOLOMEW, 1987). It is a side reaction were free fatty acids, particularly in the absence of hydrogen and in the presence of water reacts chemically with nickel to form Nickel soaps (BIRD *et al.*, 1979; HASTERT, 1979; SCHMIDT, 2000; ANNEKEN *et al.*, 2012; EVONIKCATALYST, 2016a). In Figure 32 is represented the nickel soap formation reaction.

Figure 32. Nickel soap formation reaction

$$Ni + 2RCOOH \rightleftharpoons Ni(OOCR)_2 + H_2 \quad \text{and}$$
$$NiO + 2RCOOH \rightleftharpoons Ni(OOCR)_2 + H_2O$$

(ANNEKEN *et al.*, 2012)

Nickel soaps are catalytically inactive and blocks the active surface of the catalyst (AUER *et al.*, 1998). When hydrogenation is performed on triglycerides this is not an issue, however, it becomes an issue when hydrolysis occurs simultaneously. On this study, water presence is imperative once hydrolysis is also part of the one-pot reaction. Evidence of this shortcoming is on the product after the reaction. In Figure 33 can be observed the green characteristic color of nickel soap dissolve in water, nickel in its oxide form is green.

Additionally a few pictures from different reactions display a green soap-like presence on the product, which would correspond to the inactive nickel.

Figure 33. Nickel soap formation on the product mixture reaction

Nickel salt dissolved in water

Green soap-like, present on the reactor vessel after the reaction

Product mixture appearance after reaction

To remove the feedstock impurity drawback from the equation, refined soy oil was tested using the same catalysts. Table 15 presents some physicochemical properties of the oil.

Table 15. Physicochemical properties of soy oil

Properties	Soy oil
Acid value (mg NaOH/g)	0,9372
Iodine value (g I/100 g)	127

The products of tests on Table 9 were analyzed and the results are on Table 16. From the initial results, an increment on the hydrogenation conversion was observed, nonetheless such increment was not considered as substantial and, again, from organoleptic perception and based on the results, saponification phenomenon was confirmed as the main issue.

Table 16. Reaction test with soy oil product analysis

Test	AI (mg NaOH/g sample)	IV (gr I/100g sample)	Extent of hydrogenation (%)
SS1	112	117	8
SS2	113	122	4
SS3*	14	112	12
SS4	120	119	6
SS5	121	125	2
SS6	123	124	2

*Hydrogen instead of nitrogen

Test SS1 and SS2 were carried out without heterogeneous catalyst and yet, the degree of conversion was higher when compared to crude palm oil. Also, both were performed with different levels of water. As was concluded on the prior test, a big excess of water is not necessary in order to achieve high hydrolysis conversion. SS3 was implemented using hydrogen instead of nitrogen to determine if the NiAl was able to hydrogenate the oil. From the analysis it can be concluded that, despite its higher conversion in comparison to the other test, it was still not significant. This was a crucial indicator that the catalyst was not working properly under the studied conditions, even when molecular hydrogen was implemented in the absence of formic acid. From the other tests can also be noticed that the increment on the water ratio decreases the hydrogenation conversion. Being an indicator that water in the presence of oil and formic acid is promoting the catalyst deactivation. Likewise, when comparing the tests without catalyst and with catalyst, the conversion is similar, which can only be explained by a deactivation on the catalyst function. Accordingly, can be implied that nickel soap formation is definitely affecting the performance of the catalyst.

Something important to mention is the organoleptic perception of the product. During this screening test was noticed that the products had a high content of formic acid, which means that its decomposition was not occurring as expected, indicating that catalyst efficiency was compromised. Since the results from the initial product characterization showed a lack on hydrogenation, not further characterization tests were performed for the products.

The one-pot hydrolysis-hydrogenation with the catalysts tested, Raney Nickel and Nickel Alumina, showed an insignificant performance, due to nickel saponification, under the studied parameters. Since both catalyst are widely use on hydrogenation reactions as showed on Section 3.3.2, it is likely that hydrolysis needs to be carried out in separated vessels from hydrogenation (HASTERT, 1979). Being that, the objective of the study is the production of saturated fatty acids in a one-pot reaction a decision on a new catalyst an oil was indispensable.

Therefore, to overcome such drawbacks and reach the objectives of the dissertation thesis a new set of test called target test was implemented. Crude palm oil was replace with refined palm oil (RPM) and the catalysts were replaced with an active Nickel Silica catalyst, especially designed to avoid nickel saponification.

5.2.2 Target tests

5.2.2.1 Feedstock characterization

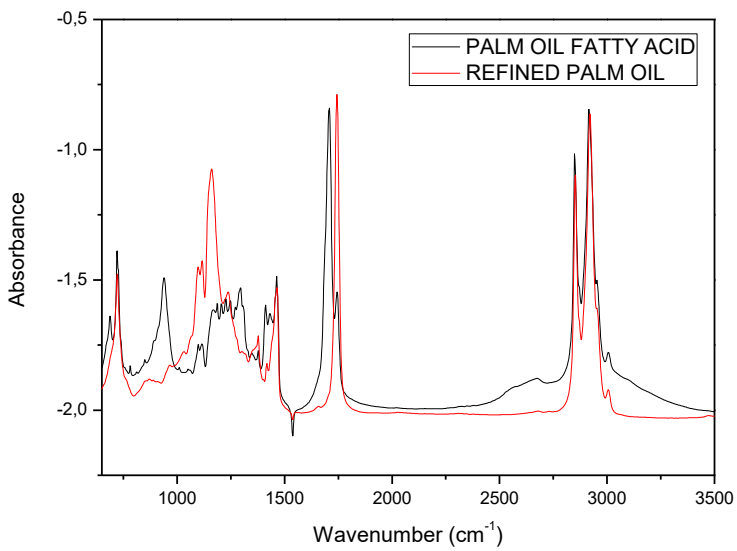
For these tests, two feedstock were used: refined palm oil (RPO) and palm oil fatty acid (POFA). Table 17 shows some physicochemical properties of the oils.

Table 17. Physicochemical properties of RPO and POFA

Properties	Refined palm oil	Palm oil fatty acid
Acid value (mg NaOH/g)	0,43	117,18
Free fatty acid (% oleic)	0,3	82,6
Iodine value (g iodine/100 g)	51	49

In Figure 34 is the overlapped infrared spectrum of the refined palm oil and the palm oil fatty acid, where is represented the absorption bands characteristics for the functional groups (SILVERSTEIN *et al.*, 2014) contained in each sample. In order to analyze the spectrum, it was divided in two regions. The first region is the fingerprint in the interval from 650-1500 cm^{-1}, and the second is the functional groups region from 1500-3200 cm^{-1}.

Figure 34. IR spectrum for RPO and POFA



Based in the literature (CHE MAN *et al.*, 1999; CHRISTY & EGEBERG, 2006; PEÑA *et al.*, 2014; SILVERSTEIN *et al.*, 2014) the most relevant bands for both feedstocks were identified, as can be seen on Table 18.

Table 18. Relevant IR absorption bands for RPO and POFA

Region	Band (cm^{-1})	RPO intensity	POFA intensity	Attribution
Fingerprint	680-725	Medium low	Medium low	*Cis* HC=CH stretching
	941	-	Medium	*Trans* HC=CH stretching
	1097-1116	Low	Low	O-CH2-C stretching
	1340-1390	Medium low	-	O-CH2 symmetric bending
	1400-1475	-	Medium	O-H bending
	1464	Medium	-	CH(CH2 , CH3) bending
Functional group	1707	-	Very high	OH-C=O stretching
	1744	Very high	Medium Low	C=O stretching
	2851	High	High	CH2 symmetric stretch
	2920	Very high	Very high	CH2 asymmetric stretch
	3008	Low	Low	*Trans* =CH stretching
	3025	Low	Low	*Cis* =CH stretching

The fingerprint region shows characteristic and unique bands for every compound that produces a unique pattern in this area. Therefore, identity can usually be confirmed by comparison of this region to a known spectrum or with complementary tests. The objective of the test was not to characterize the whole molecule, but rather to recognize the functional groups to identify the formation of fatty acids and double bonds behavior.

The RPO fingerprint region displays a content of cis alkene at 680-725 cm^{-1} stretching vibration and a symmetric bending band at 1340–1390 cm^{-1} which corresponds to the functional group O-CH2 in the glycerol moiety of triglyceride, diglyceride, and monoglyceride in the palm oil. On the functional group region is identified the C=O stretching absorption of the triglyceride ester linkage at 1744 cm^{-1}, and the CH absorption in region from 2800-3000 cm^{-1} that corresponds to CH2 symmetric stretch vibration band, and finally a low =CH stretching vibration bands at 3008 cm^{-1}.

Spectrum for POFA shows in the fingerprint region the presence of *cis* and *trans* alkene and the stretching vibration band 1400–1475 cm^{-1}, corresponding to the functional group carboxylic acid. The functional group region is composed by the OH-C=O stretching vibration band at 1707 cm^{-1} , a lower band in C=O stretching absorption corresponding to the triglyceride compound at 1744 cm^{-1} and the CH symmetric and asymmetric stretching vibration band at region from 2800-3020 cm^{-1} (*cis* C=CH, CH2, CH3, CH2/CH3 stretching bands), and finally . The bands identified for every feedstock were consistent with the expected composition.

TLC (Thin-Layer chromatography) analysis was additionally performed to identify the main compounds present in every sample. In Figure 35 and Figure 36, the chromatogram of the analysis is displayed.

Figure 35. TLC for refined palm oil

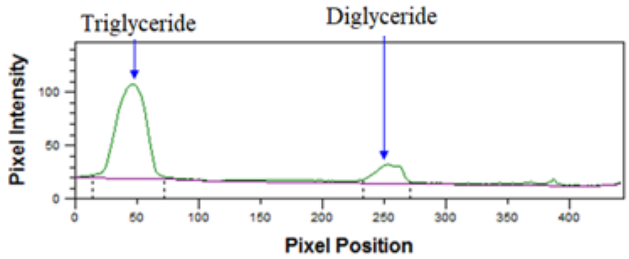
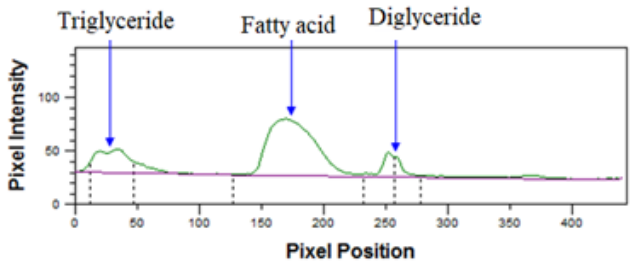


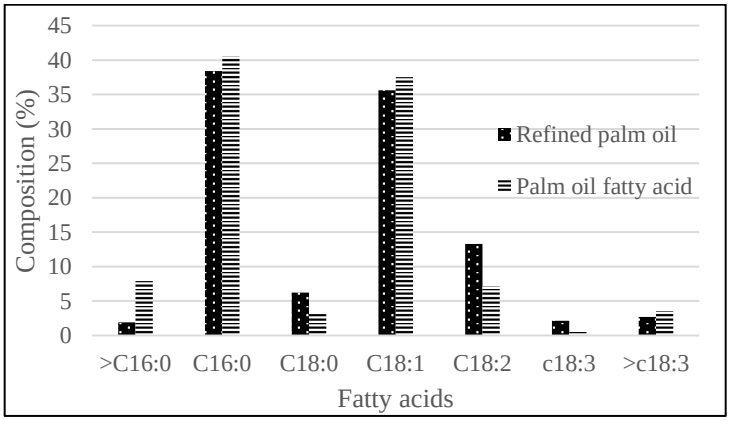
Figure 36. TLC for palm oil fatty acid



As expected, the RPO shows a high composition of triglycerides, however it was also identified the presence of diglycerides. On the other hand, the highest composition of the POFA is fatty acid with a low presence of triglyceride and diglyceride.

Once the main functional groups and compounds were identified, an additional test to determine the fatty acids composition was carried out with the Gas Chromatography with Flame-Ionization Detection (GC-FID) analysis.

Figure 37. Fatty acid composition of RPO and POFA from the GC-FIC analysis



The results of the test showed in Figure 37, displays an oil composition of 39% of palmitic acid (C16:0) and, 6,2% of stearic acid (C18:0), 36% of oleic acid (C18:1), and 13% of linoleic acid (C18:2). It can also be observed a low composition of linolenic acid and other components lower than C16:0 and higher than C18:3. Such results are consistent with the composition reported in literature. The POFA composition is close to the RPO. Slight differences are noticeable due to the margin of error of the test, the different batch of feedstock, the FAME conversion error and dilution error.

As said before the main test to monitor the hydrolysis and hydrogenation progress were the acid value and iodine value analysis. Withal, additional tests assists to support the results and give a better representation of the feedstock composition for further comparison with the product samples.

5.2.2.2 Product characterization

With the new feedstock and catalyst, twelve target tests were performed. Based on the results of the screening tests, it was observed that a big excess of water is not necessary to achieve a high degree of hydrolysis conversion, therefore a 5:1 molar water:oil ratio was selected for this set of tests. The target tests were carried out under the following conditions: 190°C, 750 rpm, 20 bar of initial pressure, 4 hours of reaction time, formic acid as hydrogen donor and homogenous catalyst, NiSi as heterogeneous catalyst and 3 wt% of heterogeneous catalyst loading.

The sequence of tests were accomplished to enlighten the performance of the reaction. Besides the AI and IV parameters to monitor the progress of the reaction, the system's pressure during the whole reaction was also observed, once the pressure on the vessel suggests the decomposition of the formic acid into hydrogen and carbon dioxide. This will be further discussed. Pressure on the system was always autogenous.

Below, the analysis of the test results on Table 10 is divided on two sections. One representing the monitoring product analysis and the other the additional analysis.

- Monitoring product analysis

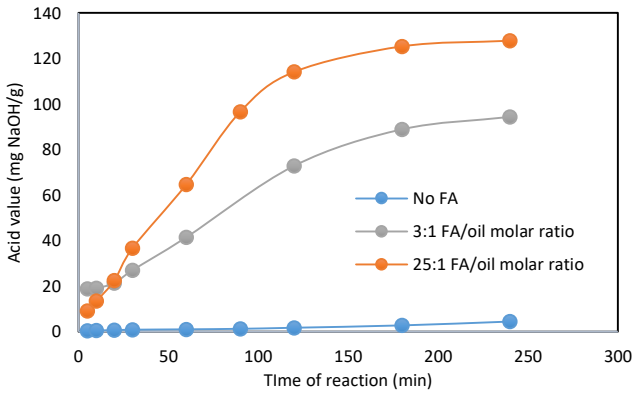
As mentioned before, in order to monitor the progress of the reaction, acid value (AV) and iodine value (IV) were measured as shown on Table 19.

Table 19. Results of monitoring product analysis

Reaction type	Test	Acid value (mg NaOH/g)	Iodine value (g I_2/100 g)	Extent of hydrogenation (%)
Hydrolysis kinetic curve w/o heterogeneous catalyst	1	8	N/A	N/A
	2	98	N/A	N/A
	3	129	N/A	N/A
Hydrogenation w/o formic acid	4	2	1	98
	5	7	1	98
Influence of formic acid in hydrogenation	6	84	20	62
	7	125	18	66
Reaction time one-pot reaction	8	82	20	62
	9	79	18	66
Fatty acid hydrogenation	10	125	19	64
	11	126	19	64
	12	136	19	64

The first three test (Test 1-3) aimed at understanding of the hydrolysis kinetic using formic acid as homogenous catalyst with three levels of formic acid. No heterogeneous catalyst is present on this test. On Table 19 is displayed the AI and IV parameters for the last aliquot of every reaction. The kinetic curve was plotted by taking aliquots at different times throughout the reaction at 5, 10, 20, 30, 60, 90, 120, 180 and 240 minutes as shown in Figure 38.

Figure 38. Hydrolysis kinetic curves



The first reaction (Test 1) was a blank test without homogeneous catalyst. As expected, the hydrolysis conversion was pretty low. On the other hand, when FA is used as homogeneous catalyst (Tests 2 and 3), the conversion is higher, and the higher the catalyst ratio the better its performance. This results shows the high efficiency of the FA as catalyst for the hydrolysis

reaction under the studied conditions. Additionally, it can be seen that, at 180 min, the hydrolysis reaction achieves its higher conversion and stabilizes.

Test 4 and 5 aimed to validate the performance of the new heterogeneous catalyst under the reaction conditions in a typical hydrogenation reaction, using molecular hydrogen without formic acid. The goal was to determine the extent of hydrogenation of the catalyst. Furthermore, Test 5 was carried out under the presence of water to determine its influence on the product. As it can be seen on Table 19, even under the presence of water, the catalyst has an extent of triglycerides hydrogenation of 98%, and no Nickel saponification or deactivation was observed. Also, as expected, no hydrolysis conversion occurred due the absence of hydrolysis catalyst. Establishing that, the selected catalyst is suitable for carrying out the hydrogenation reaction under the studied parameters.

Entries 6 and 7 were performed under the same conditions at different formic acid levels. The higher level, 25:1 molar ratio FA/oil, showed a better performance regarding hydrolysis conversion. However, the extent of hydrogenation for both entries are alike. For entry 6, an IV=20 is obtained, and for entry 7, an IV=18 is obtained. Taking into account that, according to the method for IV determination (AOCS Tg 1a-64), a ±4,6% g I2/100 g margin of error exists. Which could mean that both extent of hydrogenation are equals or slightly different.

On Test 8 and 9 the objective was to determine if the reaction time had an influence on the hydrogenation conversion. According to RUPPERT *et al.* (2015), the hydrogenation does not begin until all formic acid available is completely decomposed in hydrogen. For this reason, the reaction was tested at different time lengths, with the lower formic acid level, 3:1 molar ratio FA/oil and under the same parameters. Test 8 was performed during 10 h and Test 9 during 48 h. Acid value remains consistent through time.

In addition, throughout the length of reaction, the pressure continued to build up. The increment on pressure was due to the continue decomposition of formic acid. For the 48 hours of reaction, the increase rate of pressure started to diminish, but it did not stop. The final pressures at the end of every reaction at 4, 10 and 48 hours were respectively 45, 61 and 93 bar as will be shown further. Interestingly, despite the long reaction time, the extent of hydrogenation seems to remain unchanged. This can be explained because of the deactivation of the heterogeneous catalyst through time or the lack of hydrogen in the environment to perform the hydrogenation.

To overcome the second issue mentioned, a different feedstock was used: palm oil fatty acid (Acid value of 117 mgNaOH/g). This was made with the intention of leaving more formic acid available for decomposition, rather than for both reactions. Test 10 and 11 were carried

out under the same conditions, without water to avoid hydrolysis. Test 10 was performed with hydrogen to determine if the stagnation on the IV was occurring because of the lack of hydrogen. Nonetheless, IV remained unchanged. One more test, Test 12, using water to pursue both reaction was performed. Hydrolysis achieved complete conversion while IV continued stagnated. With the results of this tests, it was confirmed that deficiency of hydrogen on the reaction is not the cause of the IV stagnation, but is rather related to the catalyst.

VARKOLU *et al.* (2016) expresses that some Nickel catalyst show catalyst poisoning due to the presence of water on the reactant medium, however, in this case water does not seem to have any influence on the hydrogenation reaction.

When comparing the pressures at the end of the reactions on Table 20 it can be noticed that, for Test 6, 8 and 9, such pressure increases with time. Meaning that formic acid decomposition is still ongoing. Probably, up to the point of 4 hours of reaction (maybe before), the hydrogenation process stops despite the continuous decomposition of formic acid. From Entries 10, 11 and 12 it was observed that, despite the change of pressurize gas type (hydrogen and nitrogen), no alteration on the end pressure is observed.

Table 20. Pressures at the end of reactions

Test	Pressure (bar)*
6	42,1
8	61,3
9	93,1
10	40,7
11	40,3
12	43,9

* Initial pressure: 20 bar

The results suggest that hydrogen is available on the reaction environment and, somehow, such hydrogen is not reacting with the double bonds of the fatty acids chain. This can be explained because in a heterogeneous system, the liquid must be saturated with hydrogen, and such saturation will depend on the temperature and pressure, since it will determine the solubility of the hydrogen in the system. The controlling step on the reaction could be the saturation of the liquid phase with hydrogen. Hydrogenation reactions are really complex and there are many influencing factors that determine the rate of reaction.

The hydrogenation reaction takes place on the surface of the catalysts where oil and gas molecules are adsorbed and brought into close contact. Therefore, any condition that affects the catalyst surface or controls the supply of gas to the catalyst surface will affect the course and rate of the reaction. One hypothesis is that hydrogenation occurs up to an extent before formic

acid is fully decomposed affecting the extent of reaction, as already observed on literature (DENG *et al.*, 2010; RUPPERT *et al.*, 2015). If low hydrogen concentration is present on the catalyst surface, the hydrogenation will be more selective towards polyunsaturated compounds and isomerization. Meaning that, partial hydrogenation and isomerization will occur.

The two reactions, formic acid decomposition and hydrogenation, occur simultaneously or sequentially on the catalyst, depending on the relative adsorption of the reactants. KOBE *et al.* (1991) suggest that the choice of the hydrogen donor can affect the reaction through its competitive adsorption onto the catalyst. Such competitiveness was also observed on DENG *et al.* (2010) and RUPPERT *et al.* (2015) studies.

On the other hand, VARKOLU *et al.* (2018) observed that the activity of the Nickel catalyst, when using formic acid as hydrogen donor, decreases due to the formation of carbon species through the condensation of reaction intermediates on the catalyst surface. It is also suggested that in the presence of formic acid, some catalyst have low stability due to leaching of the active phase (RINALDI, 2014).

When formic acid is decomposed at high temperatures CO production is likely to occur causing deactivation of the catalyst (TEDSREE *et al.*, 2011). Additionally, in the same extension that hydrogen is formed, CO_2 is equally produced. This could mean that CO_2 may be interacting with some active sites on the catalyst. Moreover, if on the reaction there is presence of a hydroxide (OH-) or alkoxide (RO-) it can combined with CO2 to form bicarbonate. (RAJAGOPAL *et al.*, 1994). The bicarbonate might increase the basicity of the medium and also reduce the activity by physically blocking the catalytic sites. Since there are a multiple reactions occurring simultaneously, intermediate and side reactions are likely, and are important to consider.

The catalyst selected, NiSi, in presence of triglyceride or fatty acid, with no formic acid, shows a high selectivity towards hydrogenation as was shown on Test 4 and Test 5. Therewith, the hypothesis of the stagnation is a possible deactivation/poisoning or blockage of the active sites of the catalyst, or competitive adsorption of the species on the catalyst, caused by the hydrogen donor.

To better understand the behavior of the reaction co-products are necessary to be studied. Additionally, to validate the deactivation of the catalyst, additional test and analysis of the used catalyst are important.

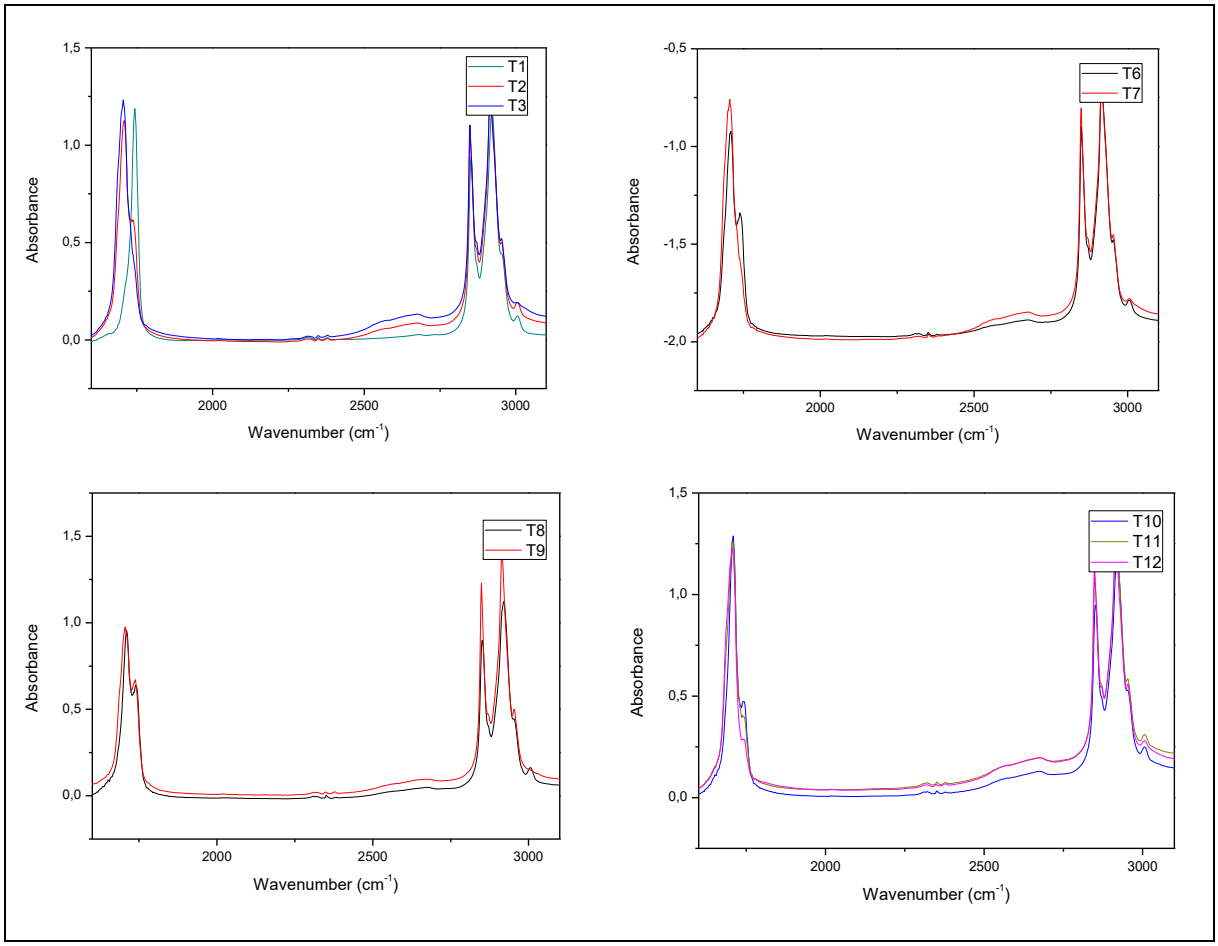
➢ Additional product analysis

Since the objective of this additional test was not to create a full representation of the product molecule, but rather to corroborate the results of the AI and IV, a few samples were selected for analysis. Furthermore, such qualitative and semi-quantitative analysis also assists to give an idea of the main compounds presented on the samples.

- Infrared spectroscopy

With infrared spectroscopy, the conversion of triglycerides into fatty acids was stablished. However, the IR test is merely qualitative. So, for the products analysis, the focus was identifying the bands of interest. Figure 39 introduces the spectrogram of some selected samples.

Figure 39. Infrared spectroscopy of product samples



As shown on Table 18, the carboxylic acid vibration band is at 1707 cm^{-1}, and the triglyceride stretching vibration band at 1744 cm^{-1}.

For T1-T3 it can be clearly seen the peak corresponding to triglyceride, disappearing with the increase of formic acid presence on the reaction. The peak conversion into fatty acid confirms the AI calculated for all three tests.

Spectrum of Test 7 shows as intense band on the fatty acid region, and low presence of triglyceride. As for T6, the band of triglyceride is noticeable and fatty acid band is less intense. Again, consistent with the AI calculated.

All of the other tests analyzed in comparison with the feedstock, and the IV and AI calculated for the products, are coherent with spectrum obtain on the infrared spectroscopy analysis.

- Thin-layer chromatography

When hydrolysis occurs, two step happen before the total conversion of triglycerides on fatty acids. One mole of triglyceride required three moles of water to hydrolyze. First, the triglyceride is converted into diglyceride, then the diglyceride into monoglyceride and finally into fatty acid (SUEN & CHIEN, 1941; ANNEKEN *et al.*, 2012). Thin-layer chromatography (TLC) is a commonly used technique to identify compounds based on the retardation factor (KRELL & HASHIM, 1963). This analysis was performed with a merely qualitative purpose to identify the main compounds on the samples (triglyceride and fatty acid) and the intermediaries of the hydrolysis reaction (diglyceride and monoglyceride). Through this technique, only unsaturated compounds can be spotted on the plate. Therefore, the lower the intensity, the lower the concentration of the unsaturated compounds on the sample.

On Figure 40 corresponding to Test 1, where no formic acid is added, can be seen a really low content of fatty acids and a high content of triglyceride, which is in accord to the AV calculated. It can also be spotted a few diglyceride content on the sample.

TLC chromatogram from Test 4 in Figure 41, shows a really low, almost null, concentration of all components. This means that, there is a low concentration of unsaturated compounds on the sample. This corroborates the IV calculated, that suggested high hydrogenation, therefore, high saturation.

Figure 40. TLC for Test 1

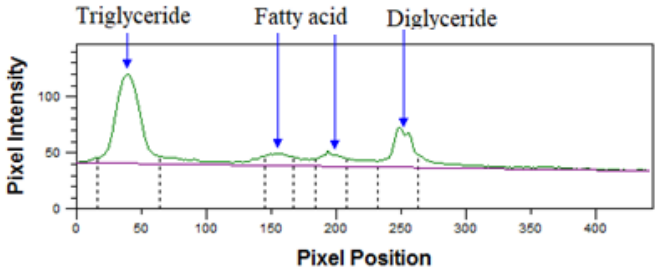
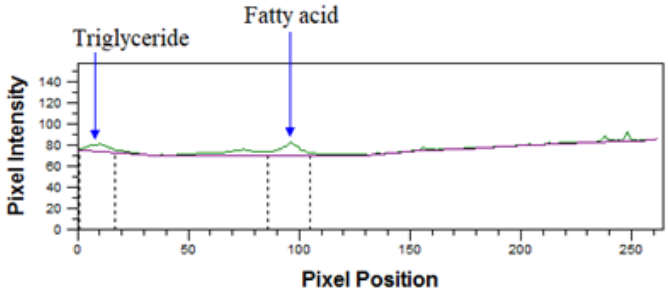
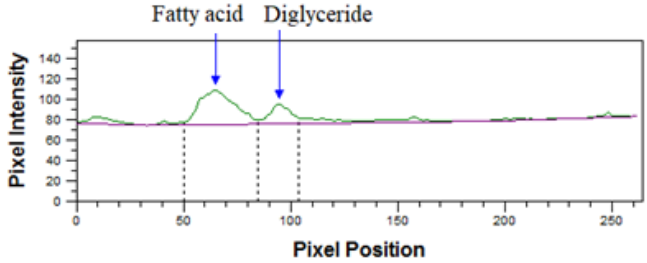


Figure 41. TLC for Test 4



In Figure 42 can be detected that, Test 7 with a high AV, has null content of triglyceride on the chromatogram, and a high intensity corresponding to fatty acid. Also a few content of diglyceride is detected.

Figure 42. TLC for Test 7



From this analysis can be concluded that TLC helps to identify the presence of intermediary molecules of the hydrolysis, such as diglyceride and monoglyceride in a qualitative way. It also helped to confirm the results on the previous analysis.

- Gas chromatography

Gas chromatography was mainly pursued to determine the composition of the fatty acids (represented as FAME) on the feedstock and the products. Since the objective of the reaction is the saturation of the double bonds, mainly represented by oleic acid, were identified the fatty acids of interest for this study: palmitic (C16:0), stearic (C18:0), oleic (C18:1) and linoleic (C18:2). Table 21 shows the composition of the main fatty acids on some product samples. The results of the gas chromatography on Table 21 are coherent with the IV showed on Table 19.

Table 21. Main fatty acids % composition of selected test

Fatty acid	RPO	Test 3	Test 4	Test 7
C16:0	39	39	37	40
C18:0	6	7	46	21
C18:1	36	34	0	34
C18:2	13	10	0	0

As can be inferred from the table, Test 3 has a similar composition to the RPO, this is consistent since on this reaction no hydrogenation was pursued. On the other hand, Test 4 shows a complete conversion of the unsaturated fatty acids, oleic and linoleic, into stearic acid, confirming the IV calculated, and the hydrogenation of the reaction. Meanwhile, Test 7, indicates a high conversion of the polyunsaturated fatty acids to monounsaturated and saturated ones. Suggesting that no complete hydrogenation was achieve on this test, which is consistent with the results of the IV from Test 7. It can also be inferred that the product from Test 7, the test with the better performance on hydrolysis and hydrogenation, is a blend of mainly saturated fatty acid, but also a substantial amount of unsaturated oleic acid is found.

From this section can be concluded that all additional tests performed helped to corroborate the results of the monitoring tests.

6 CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

The objective of this research was to obtain a blend of saturated fatty acids, from refined palm oil, without the use of molecular hydrogen and using formic acid as internal hydrogen donor in a one-pot hydrolysis-hydrogenation reaction.

The performed reactions used $NiAl_2O_3$ catalyst, prepared in laboratory, and commercials Raney Nickel and $NiSiO_2$ catalyst. The results from the catalyst characterization helped to understand their behavior and stability.

Screening tests using crude palm oil and soy oil showed a good hydrolysis conversion, represented by the acid value, when carried out with formic acid as homogenous catalyst. Nonetheless, the commercial Raney Nickel and $NiAl_2O_3$ catalyst, used to perform the catalytic transfer hydrogenation, showed poor efficiency. The lack of hydrogenation was caused by nickel saponification, a side reaction were free fatty acids in the presence of water reacts chemically with nickel to form nickel soaps, deactivating the catalyst. Although both catalyst are widely used in industry and in the literature to pursue hydrogenation of oils, it was concluded that they are not suitable in a one-pot hydrolysis-hydrogenation reaction.

It was also found that, to achieve a good extent of hydrogenation, the oil needs to be free from impurities that can compromise the efficiency of the catalyst. Additionally, the presence of beta-carotenes from the crude palm oil can compete for consuming the hydrogen available.

In order to avoid the observed drawbacks refined palm oil and commercial $NiSiO_2$ catalyst, especially designed to resist nickel soap formation, were used in the next phase of the study. High hydrolysis conversion was obtained, confirming the good efficiency of formic acid in the catalysis process. The different products were analyzed with infrared spectroscopy, thin-layer chromatography and gas chromatography.

The best conditions for the hydrolysis reaction were 25:1 molar ratio of formic acid/oil, and 5:1 water/oil molar ratio, conditions were more than 90% of the triglycerides were converted into fatty acids in approximately 180 min.

$NiSiO_2$ catalyst was tested in a classic hydrogenation reaction, using molecular hydrogen, to evaluate the extent of hydrogenation that could be achieved with such catalyst. Results showed a 98% hydrogenation of the refined palm oil with an iodine value of 1 g I_2/100g,

confirmed by thin-layer and gas-chromatography analysis. On the GC-FID results, it was observed that the product was a mixture of palmitic acid and stearic acid, with no unsaturated compounds, confirming the good performance of the catalyst in a classic oil hydrogenation reaction. However, when formic acid is used as internal hydrogen donor, an average iodine value of 19 gI_2/100g and an extent of hydrogenation of 64% was obtained, indicating partial hydrogenation. Two levels of water and formic acid, and three different reaction time, were studied to determined its influence on the extent of hydrogenation, and it was found that neither of those have a significant impact on the iodine value reduction. From the GC-FID results, it was observed a selectivity towards hydrogenation of polyunsaturated fatty acid chains and low conversion of oleic acid.

There are different hypothesis to explain the stagnation in the hydrogenation reaction. It was found that the stagnation was not caused by a lack of hydrogen in the environment, and likely to poor solubility of the hydrogen in the liquid phase. Another hypothesis is the deactivation/poisoning of the catalyst caused by side reactions, or due a blockage of the catalyst active sites with formic acid molecules cause by the competitive absorption on the catalyst. Further analysis of the used catalyst need to be performed to confirm such hypothesis. In addition, to better understand the behavior of the reaction, co-products analysis are necessary.

This one-pot hydrolysis-hydrogenation of palm oil study found that formic acid is an excellent homogenous catalyst for the hydrolysis reaction, and a suitable hydrogen donor for the partial hydrogenation of palm oil when NiSiO2 is used as catalyst.

In Brazil, the largest crops of palm oil are located in remote areas, where the access to molecular hydrogen to produce saturated fatty acids is precarious or inexistent. Saturated fatty acids have a great commercial value and application on different industries. This research is a proof of concept to show that catalytic transfer hydrogenation using formic acid is possible. Furthermore, the one-pot reaction, using a hydrogen donor, has great potential to overcome the molecular hydrogen accessibility issue and be applied on industrial scale, creating a promising business opportunity.

6.2 FUTURE WORK

- Perform a more complete GC-FID chromatography analysis to identify the formation of trans-isomers and other products.
- Perform the catalyst characterization of the used catalyst with different techniques to validate the hypothesis of catalyst poisoning and deactivation.
- Carry out a quantitative infrared spectroscopy analysis of the product samples
- Carry out a technical-economical study of the project.
- Analyze the co-products of the reaction.
- Test the reaction with a noble metal catalyst as Ru and Pd.
- Test different conditions with an experimental design to improve the extent of hydrogenation of refined palm oil.

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