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<u>Hydroisomerization of waste lipids: improving the quality of</u> <u>biofuels and production of value added-chemicals</u>

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Hydroisomerization of waste lipids: improving the quality of biofuels and production of value addedchemicals

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Declaration

I declare that the submitted text is the result of the three years of research composed solely by myself and has not previously been proposed to obtain a degree. I declare also, all the works done or published by others has been fully referred. Moreover, collaborations and consultations are totally referred and acknowledged, too. Parts of this thesis have been extracted to publish in international journals in favor of RE-CORD, INNOVHUB-SSI srl, and university of Florence.

> *Maghrebi Ramin* Florence, October 2020

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List of symbols and acronyms

+BPAME	Branched palmitic and longer methyl esters
BFAs	Branched short-chain, long-chain, saturated and unsaturated fatty acids
BLCSFA	Branched long-chain saturated fatty acids
BLCUFA	s Branched long-chain unsaturated fatty acids
BMOs	Branched methyl oleates
BOAs	Branched oleic acids
BSAs	Branched stearic acids
BSAMEs	Branched stearic acid methyl esters
BUFAs	Branched unsaturated fatty acids
CFP	Cold flow properties
CFPP	Cold filter plugging point (°C)
СР	Cloud point (°C)
C/F	Catalyst-to-Feed ratio
GHSV	Gaseous hourly space velocity, e.g., the volume of gas/ volume of catalyst/hour
HVO	Hydrotreated vegetable oil
LA	Linoleic acid
LCAs	Long-chain alkanes
LCSFAs	Long-chain saturated fatty acids
LCUFAs	Long-chain unsaturated fatty acids
LHSV	Liquid hourly space velocity, e.g., the volume of liquid/ volume of catalyst/hour
MO	Methyl oleate
MP	Melting point (°C)
NM	Not mentioned
OA	Oleic acid
PFAD	Palm oil fatty acid distilled
RES	Renewable Energy Sources
SAME	Stearic acid methyl ester
WHSV	Weight hourly space velocity, e.g., the weight of substrate/volume of catalyst/hour

Summary

Residual linear long chain saturated fatty acids derived from lipid-based feedstock industrial processing have a high potential to power up sustainability by being used in the bio/green fuel and chemical industries. These renewable raw materials can have a wide variety of applications in either field after required treatment. For instance, after esterification and a subsequent branching, branched fatty acid methyl esters can be produced. These products can then be blended in higher percentages than the current allowed percentage of 5 or maximum 10. There are other potential applications such as production of aromatics namely benzene, toluene, and xylene (BTX) that are currently produced from fossil resources. In addition, after some structural modifications, these fatty acids can be even a good match for cosmetics applications. However, the most important obstacle for using long chain saturated fatty acids is their tendency for crystallization and solidification at temperatures higher than the ambient temperature. This defect and how to overcome it was the focus of this work through a process known as hydroisomerization.

The scope of the present study is first based on a systematic theoretical study on the hydro/isomerization of long chain unsaturated fatty acids, long chain saturated fatty acids, and long chain hydrocarbons. Then, a subsequent experimental part tests the performance of different catalysts in order to identify the most promising process pathways, materials and working conditions. In conclusion, a final model based on the results from the experiments is developed to represent a biodiesel plant modified by a hydroisomization unit. The main goal of this research is to improve the cold flow properties of biodiesel by branching the linear long chain saturated fatty acids to interfere with crystal packing. Since branching is an acid-catalyzed reaction by its nature, the heart of this work is catalytic experimental trials in order to screen the promising catalysts and expand in the most promising catalyst.

The first chapter primarily introduces the long chain saturated/unsaturated fatty acids as well as the advantages of using them to aid sustainability. Then, it explains the application, theory, and mechanism of branching. Moreover, it reviews comprehensively three sectors; isomerization of long-chain saturated fatty acids, of long-chain saturated fatty acids, and of long-chain alkanes while investigating the state of the art in each sector. Hence, catalysts and the operating conditions are extracted from previous works. Finally, through a comparison between the three sectors, a proposal will be made. This proposal is mostly based on the data in more investigated sectors, i.e. long chain alkanes and long chain unsaturated fatty acids. The final goal of the proposal is to power up the research in the weakest field out of the three, i.e. long chain saturated fatty acids.

The second chapter presents the materials and methods for the whole experimental campaign. Firstly, chemical substances used for the whole parts are introduced. Secondly, procedures by which different catalysts were prepared and characterized are explained. Thirdly, two experimental set-ups that were used for performing the batch experiments will be described followed by the experimental procedure for each of the set-ups including the final product extraction method. At the final section of Chapter 2, analytical methods containing five techniques such as: GC-MS, GC-FID, acid value, Micro-GC, and melting point analysis will be explained for further interpretation of the data.

Chapter three describes the structure of the experiments that were categorized on the basis of the type of catalyst. The first part is divided into 4 subcategories explaining the experiments with Pt-H-Beta catalyst. These subsections show the logic behind the designed experiments such as the replication experiments, two DOEs, and the final single experiments. In the second part, the type of catalysts and the operating conditions investigated will be defined. Chapter four reports and discusses all the results from the experiments. In this chapter, results of the experiments on Pt-H-beta will be presented and discussed by explaining the effect of various parameters on the catalyst performance. In addition, results from the screening experiments on 4 zeolites without metal impregnation, a Friedel-Craft catalyst, and a non-noble metal loaded zeolite will be reported and discussed. In the end of this chapter, the best result will be investigated in more details.

Chapter five presents the modelling of a biodiesel plant modified by a hydroisomerization unit to define the "Energy demand" of the industrial scale plant and a subsequent economic assessment. This chapter includes the mass and energy balance as well as the technoeconomic analysis of the industrial-scale model. For this model, a specific software equipped with updated as well as comprehensive database on chemical compounds including branched desired compounds has been utilized.

1 Isomerization of long-chain fatty acids and long-chain hydrocarbons

1.1 Introduction

Although biodiesel production cost is highly dependent on the feedstock price (rapeseed and sunflower oil, etc.), which usually accounts for approximately 75% of the entire production costs that includes, direct labor, chemical feedstock, general overhead, energy, and depreciation [1], [2]. This situation leads industries to look for the most economic feedstocks, such as palm oil, or those offering premium prices for the produced biodiesel, such as waste oil, used cooking oil, lard, tallow, or poultry fat [2]–[5]. Moreover, biodiesel produced from palm oil and waste animal fat can have superior oxidative stability and high heating value [6]. Besides, many studies confirmed that the utilization of a higher percentage of longer chain fatty acids, as well as saturated biodiesel molecules per se, causes an improved cetane index compared to shorter chain unsaturated ones [7]–[9].

However, FAME produced from these feedstocks includes high amounts of saturated compounds and thus, suffers from poor cold flow properties. This issue is of particular relevance in countries with colder climates [2], [5], [6], [10]–[12]. In particular, waste lipids, such as animal fat, or PFAD, generate FAME with poor cold flow properties. Hence, isomerization could help overcoming such biofuels cold performances.

In fact, isomerization is a promising approach to improve the cold flow properties (such as pour point, cloud point, and cold filter plugging point) by lowering the melting

point of fatty acids [2], as the molecules undergo rearrangements in their structure without adding or losing any atoms [13].

Ngo *et al.* [14] reported a noteworthy reduction in monobranched isostearic acid melting point compared to stearic acid. Moreover, a considerable superior oxidative stability was reported for FAME originating from isomerized stearic acid (40 h, as measured at 110 °C) in comparison with the FAME produced from oleic acid, which is the monounsaturated counterpart of the mother molecule (approx. 2.5 h) [15], [16]. These experimental results, clearly confirmed the BLCSAFs as an excellent reagent for esterification to produce biodiesel.

The present review first aims at explaining the isomerization and its mechanism; Then, it will investigate the research on isomerization of LCUFAs, LCAs, and LCSFAs by microporous solid acid catalysts, with/without metal sites. Then, based on the data collected from the three mentioned sections will propose promising catalysts as well as key operating parameters for isomerization of long chain saturated fatty acids. Palmitic and stearic acid have been selected as the reference feedstock to represent the most abundant saturated fatty acids in sustainable, environmentally friendly material such as vegetable oils and animal fats.

1.2 The isomerization of fatty acids

The present chapter investigates how the isomerization reaction is particularly beneficial for upgrading of fatty acids. Despite it is relevant even for paraffin hydrocarbons, in particular in the oil refining sector. The target of the review therefore aims to address the isomerization of saturated fatty acids.

1.2.1 The definition

Isomerization is a chemical reaction where the principal product is the isomeric form of the principal reactant. An intramolecular isomerization that involves the breaking or making of bonds is usually defined as molecular rearrangement [17]. As a result of the molecular rearrangement and in contrast to cracking processes such as decarboxylation or decarbonylation, in an ideal isomerization, carbon loss in the form of non-condensable gases does not happen [2]. Summarizing, the atom economy for an ideal isomerization is 100%. This parameter is calculated from the formula as follows:

Atom economy(%) = $\frac{\text{Molecular weight of product}}{\text{Molecular weight of reagents}} \times 100 [18]$

This originates from the rearrangement of the atoms of the molecules compared to bond cracking.

Moreover, other indexes in green chemistry metrics, are reaction mass efficiency [19]:

Mass efficiency(%) =
$$\frac{\text{Mass product}}{\text{Total mass reagents}} \times 100$$

and Carbon efficiency:

Carbon efficiency(%) =
$$\frac{\text{Quantity of carbon in product}}{\text{Quantity of carbon in reagents}} \times 100$$

Likewise, mass and carbon efficiency are 100% in an ideal isomerization due to the nature of the process.

1.2.2 Properties of isomerized fatty acids

In addition to the fuel sector, isomerization also provides the opportunity to convert long-chain saturated fatty acids to other value-added products [14] such as lubricants, cosmetics, fabric conditioners, and surfactants are some examples [20], [21], as well as paint driers [22], vinyl stabilizers, and cosmetics [23].

Isomerized fatty acids are biodegradable [24] rather than fossil-derived products. Biodegradability makes these products perfect candidates for replacing traditional lubricants and cosmetics [25]. This compatibility happens for a variety of reasons. Low pour point, high viscosity index, high thermal and oxidative stability, low surface tension (which leads to high wettability¹), high solubility of corresponding salts in aqueous and organic solvents, low packing density to high water vapor permeability, and high spreadability could justify this claim[24], [26]–[29].

Isostearic acid, nowadays, is one of the most common isomers from fatty acids. Currently, this valuable product is produced through a multi-step process depicted in

¹ Wettability stands for the property of a liquid whereby its **spreadability** on a surface is measured [196]

Figure 1. However, this process suffers from low production yields.



Figure 1. Current process for the production of isostearic acid [20]

Isostearic acid (IA) is a well-known example that can be used both in the production of biofuels and consumer products [14]. Stearic acid has a melting point of 69 °C, while IA has a melting point below 5 °C. Apart from its excellent cold flow properties and biodegradability, IA is also non-toxic. This product is predominantly used in cosmetic industries since it is odorless and having moisturizing effects. The latter favors the smooth spreading of body creams on the skin [30]. Furthermore, IA can be used in two-cycle engine oil to lower the pour point of the fuel [23].

However, the demand for it has increased to a great extent as a versatile product rather than as a co-product. As such, action needs to be taken towards a robust exclusive production plan from more sustainable and economical starting material [20].

1.2.3 The difficulties to isomerize SFAs

Nevertheless, three reasons makes branching saturated fatty acids challenging. First, Ngo et al. [31] reported a more hindrance towards isomerization of a mixture of fatty acids by solid acids, when there was a predominant share of saturated fatty acids. The limiting effect of saturated fatty acids stems from a lack of double bonds in their hydrocarbon chain. Lack of double bonds means the impossibility to easily create carbocations by an acid, the latter being essential for isomerization reactions. Therefore, the mere use of solid acids for the isomerization of fatty acids should not be effective. Second, for many years, the research has been focused on the isomerization of unsaturated fatty acids although a few researches have addressed the challenge when saturated fatty acids are used as a feedstock for branching reactions [2], [12], [21].

Third, compared to short-chain compounds, the isomerization of long-chain compounds is more delicate since long hydrocarbon chains tend to crack faster than shorter ones leading to lower selectivity and therefore lower yields [32].

1.2.4 Branched Saturated fatty acid

Branched saturated fatty acids exist in nature in a wide variety of forms. The presence of isomerized as well as trans fatty acids in ruminant and milk fats does not depend on biosynthesis, but from the activity of rumen bacteria, able to hydrogenate or isomerize fatty acids. Although, in comparison with other compounds they are often present as a minority, in bacteria their share is even more than the unsaturated fatty acids. Nature-synthesized isomers that have the methyl group on the penultimate (iso compounds) and antepenultimate (ante-iso compounds) carbons, are the most frequent branched compounds (Figure 2) [33].



Figure 2. Chemical structure of the most common occurring fatty acids in nature: iso- (on the left) and anteiso- (on the right) [33]

In addition, poly-branched fatty acids also occur mostly in animal tissues (especially ruminant animals), preen glands of birds, and bacteria. One of the most wellknown molecules belonging to this category is 3,7,11,15-tetramethylhexadecanoic acid also known as phytanic acid.



Figure 3. 3,7,11,15-tetramethylhexadecanoic acid (Phytanic acid)

1.3 Isomerization: Theory, Applications, and Mechanism

This chapter reviews the chemistry behind the isomerization, before entering into the details of each investigated feedstock, dedicated catalysts, and operating conditions.

1.3.1 Isomers classification

Isomerization is classified into two main categories which are the structural and spatial isomerization and their subcategories (presented in Figure 4). This classification applies for any chemical compound. Hence, although, the illustrated examples (Figure 4) are short chain hydrocarbons and their derivatives to simplify the manuscript, this categorization is the same for isomerized LCSFAs.



Figure 4. Isomerism types and their examples [34] [35]

As regards Figure 4, a generic fatty acid such as hexadecanoic acid has 327,216 stereoisomers as well as 876 structural isomers, while for stearic acid (with just 2 additional carbon atoms) 2,944,414 and 2,475 respectively [36]. When these transformations modify the original molecule, a lot of physical and chemical properties are affected. In general, when isomerization occurs, cold flow properties of the initial fuel could be both improved (skeletal isomerization) or worsened (geometrical isomerization). Considering the different types of isomerization (summarized in Figure 4) the focus of the present literature review is on chain/skeletal isomerization. In other words, the focus is on the type of isomerization reactions that induces molecular rearrangement. The latter involves the migration of a methyl branch from the main

hydrocarbon chain so that it forms a non-linear branched molecule from a linear mother molecule; whether in long-chain hydrocarbons or in long-chain fatty acids.

1.3.2 Commercial applications

Isomerization has already shown commercial applications both in the renewable and non-renewable fuel production industries. Regarding renewable fuel processing, a hydroisomerization unit is generally embedded in HVO plants for upgrading fuels [37]– [39]. For instance, upgrading renewable diesel that has lower lubricity and inferior cold flow properties (in comparison with petrodiesel) can be performed by the isomerization step [40]. For renewable aviation fuel's upgrading, isomerization has been reported as an essential step after deoxygenation to reduce the freezing point, improve the octane number and ultimately, to meet the aviation fuel standard (ASTM D1655 and D7566 [41], [42]).

As for non-renewable fuel processing, hydroisomerization is applied in gasoline production when short-chain hydrocarbons (C5-C6) have to be processed in order to increase the octane number of the final blend. Enhancing the octane number via isomerization is a better alternative for the production of high-octane fuels rather than blending the fuels with benzene and other aromatics. This is due to the bans that have been issued by legislations as a consequence of the carcinogenic nature of such aromatics [43]. Regarding diesel fuel, hydroisomerization is used to dewax and improve the cold flow properties of the final product [44]. Moreover, for fuels with LCAs, hydroisomerization has reported yielding a fuel with a higher viscosity index and as a result, a fuel with improved cold flow properties [45].

Furthermore, in non-fuel applications of LCAs, among all pour point reduction processes, hydroisomerization is known as the most acceptable solution[43]. for instance, the pour point of wax is decreased following hydroisomerization [43].

Isomerization of biodiesel from LCSFAs has not gained a commercial share yet. However, Knothe and Dunn's work [16] demonstrated that the melting point of LCSFAs and their esters drops after skeletal isomerization and this falloff reaches the maximum quantity when the branch is located in the middle of the chain. Their results were in line with the study by Ngo et al. [28]. Besides, Reaume and Ellis [46] attained a 16.5 °C decrease of cloud point for the isomerized biodiesel from coconut oil compared to nonisomerized biodiesel from coconut oil.

1.3.3 Biodiesel enriched in isomers

As for biodiesel, an experimental demonstration of the blending effect of isomerized products was performed by Dunn et al. [5], leading to a significant improvement of both cloud and pour point of three different samples of biodiesel prepared from soybean, canola, and palm oil. They concluded that the most remarkable improvement occurred when 17-39 wt% of the isomerized products were blended into the biodiesel. That is in line with the results from Cason and Winans [47] on blending pure fatty acids with their isomers. In fact, while they were studying the effect of branch positions of branched fatty acids on melting point of their binary mixtures with linear fatty acids, they observed a reduction in melting point.

Moreover, blending with isomers has been proved to be a better technique than blending with unsaturated fatty acids. The experimental demonstration carried out by Reaume et al. [48] demonstrated that the cloud point of the biodiesel declined steadily by addition of saturated branched molecules of biodiesel from low to high concentration. However, the melting point of biodiesel declined by blending with unsaturated molecules only when a minimum 60 wt% of unsaturated fatty acids were blended.

The isomerization of LCSFAs rather than LCUFAs is often preferred for four reasons. First, after skeletal isomerization of the LCSFAs, the branched molecules keep the high oxidative stability of original molecules whereas after skeletal isomerization of the LCUFAs, the branched molecules maintain the low oxidative stability of the original molecules [2]. Second, after the isomerization of LCUFAs, their cold flow properties either worsen or improve slightly [48]. In literature, this phenomenon has been associated with cis trans isomerization. An example is a 29 °C increase in the melting point of methyl oleate after conversion to its *trans*- counterpart (methyl elaidate) [2], [49]. This geometric-type isomerization occurs due to the higher thermodynamic stability of trans isomers [50]–[53]. Third, when it comes to hydroisomerization, hydrogenation of LCUFAs occurs much faster than isomerization. Therefore, the melting

point increases and the positive impact of the isomerization cannot compete with this adverse impact [2], [48]. Last but not least, the high capital and operating cost are barriers to the utilization of LCUFAs as feedstocks for this process. High operating costs are generally associated with the feedstock prices, while high capital costs could be associated with the sophisticated equipment needed for separation of the by-products such as oligomers [21].

1.3.4 Isomerization alternatives

There are also other methods for improving the CFP such as alkylation and biological means.

1.3.4.1 Alkylation

Alkylation is a reaction in which an alkyl group from one molecule is added to another molecule [54]. Renewable based alkylation of FAs is a technique used to improve cold flow properties [55]. Branching via alkylation is, in fact, different from branching via isomerization, as in alkylation, branched part is an alkyl radical coming from another compound rather than the original molecule. A scheme, which resumes different addition reaction pathways is resumed in Figure 5. The high costs as well as complex procedures to achieve these processes, are still the main barriers for the case of such technique in improving cold flow properties [6]. Moreover, these techniques always need unsaturated fatty acids, which were mentioned before as an undesired initial feedstock. Furthermore, alkylation results in an increase of molecular weight worsening the fuel distillation curve. The biodiesel distillation curve as it is already located around the maximum value that can be tolerated for diesel fuel.





Non-renewable based alkylation of FAs is another technique for CFP improvement. In this regard, four different production methods from hydrocarbons and alcohols have been explained in Ullman's Encyclopedia of Industrial Chemistry [56], as shown in Figure 6.



Figure 6. Alkylation of fatty acids from hydrocarbons and alcohols

The drawbacks of this pathway, however, is referred to the capital costs and yield losses which originates from numerous process steps highlighted in Figure 7.



Figure 7. Multi-step alkylation process in comparison with two-step isomerization [21]

1.3.4.2 Biological means

Another alternative is the use of biological processes. Tao et al. [57] discovered that branching saturated fatty acid methyl esters could be performed via biological processes engineering using E. coli bacteria and a yeast named P. pastoris as producers of fatty acid isomers. Nevertheless, there is a significant work to do to apply these results for commercialization. In addition, recent research by Singh and Choudhury [58] revealed the co-production of lipids and hydrocarbons by the halophilic bacterium, strain NS12IITR. After the transesterification of the lipids, a 77% share of the total esters were reported as branched-chain esters.

1.3.5 Mechanisms of isomerization

The present paragraph focuses on reaction pathways to isomerize alkanes, which can be resumed in five steps:

(1) It is necessary to functionalize carbon-carbon single bonds. In order to achieve this goal, a metal such as platinum plays the role of promoter for dehydrogenation of an alkane.

(2) In the next step, acid transforms the intermediate olefin to a carbocation.

(3) A migration of carbon happens and as a result, branching takes place. Carbon migration has been explained by alkyl shift [59] and/or cycloproponium ion formation [60] and subsequent branching.

(4) At this point, the acid performs deprotonation.

(5) Finally, metal promotes the hydrogenation of the double bond and yields the saturated branched product. The entire mechanism is summarized in Figure 8 [10], [45], [61], [62].



Figure 8. Mechanism of isomerization of long-chain saturated hydrocarbons [63], [64]

The abovementioned scheme applies for the isomerization of LCAs via bifunctional heterogeneous microporous solid acid catalysts, which is the focus of this review.

The mechanisms for the isomerization of LCSFAs is the same as their alkane counterparts[10]. Hence, by substitution of a carboxylic group instead of R1 or R2 in Figure 8, the mechanism follows the same procedure. [55], [65], [66]

1.3.6 Kinetic studies

Kinetic studies can be useful to understand where bottlenecks are located in a series of reaction steps. For instance, Reaume [10] concluded that in the isomerization of palmitic fatty acid by bifunctional platinum doped beta zeolite, the rate-limiting step was the carbon migration after protonation. The same was reported by other studies [62,91] for isomerization of unsaturated fatty acids by solid acid catalysts, and by Ono [66] for the isomerization of alkanes. However, Oliviera and co-workers [67] suggested that for the isomerization of alkanes by a bi-metallic doped zeolites the rate-limiting step was the protonation of carbon. Although the kinetic study is not the focus of the present review, more details on this topic can be found in [68]–[86].

1.4 Catalysts for isomerization

Isomerization has been categorized as a reaction, which is carried out catalytically by acids. In other words, only acid catalysts perform isomerization [63]. The catalyst role is to lower the activation energy of chemical reactions. An equilibrium reaction such as isomerization is not an exception, and it is more crucially depending on catalyst than others. In such type reaction, catalyst also helps to perform the isomerization at lower temperatures. This results in a process that could end up with higher amounts of isomerized products and at the same time, minute amounts of cracked, polymerized, and hydrogenated side products. However, coke formation is inevitable and the consequence for it is the deactivation of the catalyst. In order to limit this problem, the reaction atmosphere is replaced with hydrogen at enhanced pressures [43]. As reported, many phenomena affect the reaction, but in general, the catalyst performance determines the efficiency of the isomerization process [87].

1.4.1 Classifications of isomerization catalysts

Isomerization catalysts have been classified by different scientists based either on catalyst composition, or the operating condition in which they showed their optimum performances. Pines [63] has divided them into two major groups: solid heterogeneous acids and liquid homogenous acids. In Pine's classification, the first group contains the Friedel–Crafts (reactive such as AlCl₃), silica-alumina, dual functional while the second group contains homogenous catalysts such as sulfuric acid. Instead, Roth [43] has considered two major groups divided by high temperature and low-temperature isomerization catalysts. For instance, aluminum chloride is a conventional representative of the first group and platinum loaded catalysts fit in the second. There are even other researchers as Hidalgo and co-workers [88] that have classified the isomerization catalysts into three groups as follows: high-temperature catalysts (fluorinated alumina), medium temperature catalysts based on microporous solid acids (zeolite base catalysts), and low-temperature catalysts (chlorinated alumina).

Similarly, Valavarasu et al. [61] have divided the categories depending on the most performant temperature of each catalyst' category, including chlorinated alumina,

metal oxides (zirconia based), and zeolites as low, medium, and high-temperature catalysts, respectively.

Another important distinction concerns the category of homogeneous and heterogeneous catalysts. Homogeneous catalysts have many benefits such as the highest activity per active site. In addition, active sites are well-defined. However, heterogeneous catalysts are often economic, recoverable, and robust [89]. This could justify why almost 90 % of the catalytic processes in the chemical industries all over the globe are heterogeneous, thus even for isomerization, they are the preferred ones [90].

1.4.1.1 New classification

Therefore, by excluding the homogenous isomerization catalysts such as sulfuric acid and considering all abovementioned categories, isomerization catalysts were categorized into three new groups:

- 1) Metal chlorides/metal oxides;
- 2) Sulfated zeolite and zeolite-like² materials,
- 3) Noble metal loaded zeolite and zeolite-like catalysts.

This new classification allows highlighting the pro and cons of each category. The first group of chlorine-containing catalysts is well-known for the highest activity and yields towards isomers. The main reason lies in the lowest operating temperatures that shift the equilibrium towards isomerization reactions, which are favored at low temperatures. However, they are highly sensitive to water and contaminants such as sulfur and nitrogen [91]–[94]. These restrictions are very stringent since only a ppm of undesired compounds can poison the catalyst and have an adverse impact on the reaction. Furthermore, they can not be regenerated and even a small loss of chlorine necessitates the addition of fresh catalyst to the system [61], [95]. Such situation also, leads to high consumption of catalyst [96]. In addition, this type of catalyst is corrosive and it causes plugging on catalyst beds. To sum up, they generally involve high operating

² Aluminophosphates such as AIPOs, SAPOs, MeAPOs, mesoporous oxide material (MCM-41,AIMCM-41, zirconia based metal oxides), Silicaaluminaphosphates (SAPO) have already shown suitable isomerization performance [135] and have been mentioned in some sources as zeolites while they would be better called "Zeolite-like" materials [101].

cost, require intense maintenance, and on top, they are not environmentally friendly [56].

The second group, unlike the first one, delivers a medium activity and has an improved tolerance towards water and sulfur of less than 20 ppm in comparison to chlorine-containing catalysts. Additionally, they are recoverable and regenerable [97]. Despite all the mentioned benefits, they generally need high ratios of H₂/feed [61] and cause H₂S emissions due to the presence of different sulfite compounds [98].

The third category, which includes noble metal-containing zeolite and zeolite-like materials, have the lowest activity among the three groups. However, they impressively tolerate water and sulfur (up to 200 ppm) [61], they are recoverable and they do not produce any wastes or emissions. Last but not least, the presence of hydrogen is not mandatory to conduct the desired process but it is beneficial to obtain optimum performance [99].

1.4.1.1.1 Zeolite and zeolite-like catalysts

Zeolites are crystalline porous materials with numerous properties depending on their composition. Their main characteristics are thermal/hydrothermal stability, selectivity towards the size and/or shape of the molecules, Brønsted acidity, and that they possess small pores on their surface [100]. The stability itself can be divided into thermal and chemical stability. The former allows operating under high temperatures with/without the presence of water. The latter allows using the catalyst for long periods without having to change or even regenerate it. The shape/size selectivity leads to the minimization of undesired products by conducting the reactants, products, and intermediates in already tailored channels. Furthermore, the Brønsted acidity favors carbocation production, which is fundamental for isomerization. Moreover, small pores on their surface give the possibility to synthesize bi-functional catalysts by introducing metal nanoparticles on the zeolite surface. These specifications altogether, make of zeolites a versatile isomerization catalyst [89].

Besides, zeolites' undeniable role has been proved since the middle of the 20th century in the petroleum and petrochemical industries [101]. In particular, in the isomerization of short and long-chain hydrocarbons, they have exhibited that they can

deliver high yields and selectivities owing to their precise morphologies as well as Brønsted acidity [95]. The use of zeolites in thermo-chemical processing derives from the oil industry, where they are widely used for hydroisomerization, hydrocracking, dewaxing, de/hydrogenation, de/hydrocyclization, and reforming of hydrocarbons [93], [102]. In recent years, with the major research focus on driving the industry towards zero or even negative carbon emissions, zeolites have shown numerous promising results in biomass conversion to fuels and chemicals [90].

However, there are a few drawbacks against obtaining the same level of process efficiency when biomass is utilized instead of fossil hydrocarbon. The first barrier is the vast spectrum of exiting compounds in biomass in opposition to fossil feedstock that leads to a complicated network of reactions. The second barrier is the poor accessibility of large biomolecules to the active sites for effective adsorption. In order to overcome these challenges, innovative research focuses on trying new zeolites as well as zeolite structure modifications to functionalize the catalysts with the renewable feedstock [101]. Here following, the isomerization processes on long chain unsaturated fatty acids (LCUFAs), long chain alkanes (LCAs), and long chain saturated fatty acids (LCSFAs) will be investigated.

1.5 Catalyst performance

In this part, catalysts were investigated on the basis of their use for three different feedstocks: LCUFAs, LCUFAs, and LCSFAs. Catalysts that have been used for every feedstock are listed from the highest to lowest yields in a table in every section. Then, cocatalysts as well as key parameters in which zeolites have been investigated for every category in the past are analyzed and explained. At the end of section 3, a comparison will be made between the three groups to present the findings of the work.

1.5.1 Isomerization of LCUFAs by zeolites

According to Carey et al. [55], the first production of isomerized products from unsaturated fatty acids dates back to 1970, when Otter [103], [104] was the first to produce a minute fraction of isostearic acid using montmorillonite clay as catalyst. The main goal was to achieve the dimerization of oleic acid, however, the presence of small amounts of isostearic acid grabbed the attention towards isomerization side reaction by solid acids. Later, Hayes [105] disclosed considerable amounts of branched fatty acids using clay catalysts. Later in 1997, Tomifuji et al. [106] and Hodgson et al. [107] demonstrated the higher performance of zeolites on skeletal isomerization of long-chain unsaturated fatty acids such as oleic acid. Hodgson et al. [107] investigated the performance of 1-dimensional catalysts on isomerization including mordenite, L-, and omega zeolite with different Si/Al ratios. Tomifuji et al. [106] highlighted the influence of water as a suitable cocatalyst. Zhang et al. [108] expanded the research to a 3dimensional zeolite named Beta. Zhang and co-workers [109] illustrated the promising results for a zeolite-like material named MAS-5. Ngo et al. [110] explored the advantageous utilization of ferrierite zeolite having an 8-10 membered ring and a 2dimensional channeling structure. Subsequently, Ngo et al. [111] attained a groundbreaking achievement by poisoning the surface of the catalyst with triphenylphosphine to minimize dimerization occurring as a side reaction. Reaume and Ellis [112] investigated the effect of isomerization on various combinations of saturated and unsaturated fatty acids by bifunctional beta zeolite. Ngo [113] and Sarker et al. [114] presented the effects of 15 new catalyst surface poisoners. Finally, Sarker et al. [115] uncovered high yields³ of isomerization when using a ZSM-5 zeolite. Table 1 shows an overview of the best results of the tracked research, divided by the highest process yields to the lowest ones towards isomers.

Feed	Product	Catalyst	Si/Al	Cocatalyst ratio (wt%)	Т (°С)	P (bar) & Gas spesification	t (h)	Yield (wt%)	Ref.
OA	BSAMEs	HFerr-Amm Feed 5	0	Water Feed 3.6, <u>Cat.</u> 7.5	260	9 Ar	8	87	[114]
OA	BSAMEs	HFerr – Amm Feed 5	0	Water Feed 3.6, TPP Cat. 7.5	260	9 Ar	24	86	[115]

 Table 1. Review of the optimal yields of isomerization/hydroisomerization using long-chain unsaturated carboxylic acids

³ Yields in this part are based on the amount of isomerized product (whether quantified by GC/MS) or reported as separated product)/unsaturated fatty acid in the feed
OA	BSAMEs	$\frac{\text{HFerr}-K}{\text{Feed}}5$		Water 3.6, TPP Feed 3.6, Cat. 2.5	260	1.5 N ₂	4	84	[116]
OA	BOAs	$\frac{\text{HFerr}-K}{\text{Feed}}5$		Water Feed 1, TPP Cat. 7.5	260	1 N ₂	6	83	[117]– [119]
OA	BSAMEs	$\frac{\text{HFerr}-K}{\text{Feed}}5$		$\frac{\text{Water}}{\text{Feed}} 3.6, \frac{\text{PS}}{\text{Cat.}} 0.5$	260	5.5 N ₂	4	83	[113]
OA	BUFAs	$\frac{\text{HFerr} - \text{K}}{\text{Feed}} 5$.9	Water Feed 1, TPP Cat. 7.5	260	1 N ₂	6	81	[120]
OA	BSAMEs	$\frac{\text{HFerr}-K}{\text{Feed}}5$		Water Feed 3.6, TPP Cat. 10	280	1.5 N ₂	6	79	[31], [111]
OA	BUFAs	$\frac{\text{HMordenite}}{Feed} 8$		$\frac{Water}{Feed}$ 2	280	18 steam	6	77	[106]
OA	BOAs	$\frac{\text{PtHbeta}}{\text{Feed}} 10$	0	-	250	32 H2+8 N2	15+ 6	74	[108], [121]
OA	BSAMEs	$\frac{\text{HFerr}-K}{Feed} 2.5$		$\frac{Water}{Feed}^2$	250	1.5 N ₂	6	71 ^b	[110]
OA	BOAs, BSAs	HMordenite Feed 5	3	-	265	1 N ₂	4	70	[122]
OA	BUFAs	$\frac{\text{HFerr} - \text{Amm}}{Feed} 1.5$	0	$\frac{\text{Water}}{\text{Feed}}1$	260	1 N ₂	6	69	[123]
MO	BMOs	$\frac{\text{Hbeta}}{\text{Feed}}$ 10	7	-	250	3.4 N ₂	2	66	[124]
MO	BFAs	$\frac{\text{Bentonite clay}}{\text{Feed}} \ 10$		<u>1,2 – dichloroethane</u> Feed 200, <u>Sobuthane</u> 60 Cat.	230	NM	2	60	[125]
OA	BFAs	$\frac{\text{Hbeta}}{\text{Feed}}$ 2	60	-	300	15 N ₂	5	50	[49]
OA, LA ^c	BFAs	Montmorillonite Feed 5		$\frac{\frac{\text{Oct}-1-\text{ene}}{\text{Feed}}}{275 \text{ molar\%}}$ $\frac{AC}{Cat.} \cdot 1$	260	NM	1.5	40	[126]
Corn	BFAME	$\frac{\text{Hbeta}}{\text{Find}}$ 4		-	260	15H ₂	6	40	[46]
oil		<u>-5wt%PtHbeta</u> Feed	2.5		300	40H ₂	16		
OA	BMOs	$\frac{\mathrm{H}-\mathrm{MAS}-5}{Feed} \ 10$	5	-	250	3.4 N ₂	5	37	[65]
Tall oil FAs	BFAs	Unactivated clay Feed 2		meq Lithium salt g Cat.	260	6	1.75	20	[105]

^a All experiments were done in batch mode.

^b The quantity was modified by the same author due to the utilization of advanced analysis techniques [111] Proron Sponge

^c 28% OA+ 62% LA

As mentioned above, different catalysts for isomerization of LCUFAs have undergone examination so far, that in this part are discussed in a more detailed way, presented based on the development of the different catalyst types.

1.5.1.1 Clay

This category includes silica/alumina catalysts that has a generic shape, in opposition to zeolites which has mainly a crystalline structure. Both materials are catalytically active and have a large surface area. They are both selective catalysts for isomerization reactions from unsaturated linear fatty acids. By utilization of clay, dimerization of LCUFAs is the main reaction that is stimulated. However, in parallel, isomerization reactions are also promoted [55]. Several experimental campaign processing LCUFAs, have been carried out using different clay catalyst types whether bentonite or montmorillonite which will be discussed below.

1.5.1.1.1 Montmorillonite clay

Michael Neuss [126] demonstrated the performance of montmorillonite as catalyst combined with activated carbon as co-catalyst for the production of branched fatty acids from unsaturated fatty compounds at 260 °C and 1.5 h in a stirred autoclave. Three different combinations of unsaturated fatty and a small share of saturated compounds were investigated. The first group contained mostly two carbon-carbon double bonds (62wt% linoleic acid) while the second group contained mostly single carbon-carbon double bonds (73wt% oleic acid). The final was a standard triglyceride category, having the same composition than group 1 (although in ester form). Among the three, the first combination had the highest yield (up to 40 wt%) based on unsaturated compounds, also reminding on indispensable role of double bonds. It is noteworthy that for this process oct-1-ene with a ratio of 2.75:1 Oct-1-ene/feed (molar) was added to the feedstock in all reactions. Hence, the feed containing free fatty acids

with multiple double bonds had higher yields of isomers rather than the feed with single double bonds or the one in ester form.

Montmorillonite clay was also used by Hodgson *et al.* [107] for the isomerization of oleic acid at 250 °C(4h, under nitrogen atmosphere) and they achieved 47 wt% yield towards isooleic and isostearic acid.

1.5.1.1.2 Unactivated clay

Bezergianni [105] disclosed up to 20 wt% yield of branched saturated fatty acids through a reaction designed for the polymerization of unsaturated fatty acids using unactivated clay as catalyst, and lithium salt as well as water as cocatalysts operating at 260 °C for 2h.

1.5.1.1.3 Bentonite clay

Foglia *et al.* [125] obtained a maximum yield of 60 wt% of branched-chain methyl stearate when using methyl oleate and isobutane as reactant while, bentonite clay was used as catalyst, and dichloroethane as a co-catalyst. Besides, without isobutane, a 29% yield was achieved using only oleic acid as reactant. Unlike the results of [126], methyl oleate showed a 6 wt% higher yield when oleic acid was used.

Among all of the reviewed processes, Hodgson et al. [107] obtained the highest yield of 47 wt% at 250 °C and 4h reaction time with montmorillonite clay. A 60 wt% isomer yield by bentonite was not considered as the highest yield of clay catalysts in this work because isobutane use coulde be considered as alkylation not isomerization.

1.5.1.2 Ferrierite

Ferrierite catalysts have a remarkable effect on isomerization. Since they have a high surface area as well as a high density of Brønsted acid sites, they present a significant isomerization activity for LCUSFAs. They can be converted to bifunctional catalysts after the addition of metals on their surface or into their internal microporous structure. Ferrierite zeolite has the general formula $|Mg_2Na_2(H_2O)_{18}|[Al_6Si_{30}O_{72}]$ -FER. It has 8-10 membered ring channels resulting in a 2-dimensional channel network [127]. This catalyst showed so far, the highest yield for isomerization of oleic acid by zeolites. Sarker et al. [114] achieved an yield of 87 wt% operating at 260 °C for 8h with an initial

pressure of 9 bar Ar. The catalyst support was H-Ferr-amm-104 and the surface was poisoned by tris-(2,4,6,-trimethyl-phenyl)-phosphane (TMSP). It should be mentioned that they attained this result after an experimental set of 16 different Lewis bases. Surface poisoning in the isomerization of LCUFAs, was for the first time presented by Ngo et al. [111] who used triphenylphosphine (TPP). They increased the yield up by 8 wt% from 71 wt%(without poisoner) to 79 wt% (with the addition of 10 wt% TPP /cat and increasing the reaction temperature to 280 °C).

Ngo et al. [110] obtained a yield of 71 wt% of chain isomerized products by H-Ferrierite-K-95 catalyst at 250 °C after 6 h of reaction time. Also, they discovered the influence of water as a cocatalyst for ferrierite zeolite. The addition of 2 wt% of water (water/feed wt%), elevated the yield by 23 wt%. Furthermore, the water turned out to be more effective than methanol and isopropanol as co-catalysts in separate runs. Wiedmann et al. [120] confirmed the superiority of water as a co-catalyst for ferrierite zeolite as compared to methanol.

Moreover, enhancing the catalyst-to-feed ratio from 2.5 wt% to 5 wt% decreased the yield by 3 wt%. This yield drop probably stems from a higher rate of dimerization. In this research, the importance of ion exchange of Ferrierite-K was also illustrated. Ferrierite-K did not show any activity for the isomerization of oleic acid [110].

Brønsted acidic sites were assumed to perform the isomerization reactions of fatty acids. The latter is attributed to the characteristics of a substance that provides H+ in reactions. While, Lewis acidity is a characteristic of substances that can receive an electron pair. Ngo et al. showed that the K⁺ form of the Ferrierite zeolite did not have any activity on the isomerization of oleic acid at 250 °C, under 7 bar of N₂, after 6 h, stirred in a batch reactor. While, the H⁺ form of the Ferrierite zeolite (protonated form), had an 82 wt% of isomerized products' yield with the same operating conditions. They concluded that Lewis acidic sites did not contribute to the isomerization reactions.

⁴ In H-Ferrierite-amm-10, H and amm show that purchased commercial Ferrierite contained ammonium (amm) as nominal cation; it was ion exchanged to the protonated form (H). Then "10", represents silicon to aluminium molar ratio.

⁵ In H-Ferrierite-K-9, H and amm show that purchased commercial Ferrierite contained potassium (K) as nominal cation; it was ion exchanged to the protonated form (H). Then "9", represents silicon to aluminium molar ratio.

Figure 9 demonstrates different methods of transformation of a Zeolite containing Lewis acidic sites into the one having Brønsted acidic sites.



Figure 9. Different methods for ion exchange [31]

However, zeolites having Brønsted acid sites do not always show isomerization performance. Depending on the operating condition, HDO could be stimulated via hydrogenation-dehydrogenation reactions. Cracking and rapid deactivation via coking might be another side reaction promoted by these materials [128], [129].

Ngo et al. [110] also proved that ferrierite was reusable for at least three cycles. However, later, Ngo and co-workers [111] claimed to have improved the reusability of H-ferrierite suggesting no change in activity and a selectivity even after 10 times utilization. They also discovered 28 branched isomers as a result of H-ferrierite activity over oleic acid by utilization of small amounts of triphenylphosphine. In another publication Ngo et al. [110] determined the contribution of the various isomers. This was done using piconyl ester derivatives of branched products detected by GC/MS. The result suggested that almost 84 wt% of the methyl branches were located on carbon number 8 to 14. 8.3 wt% share was allocated to the isomers having their branches on 2nd to 7th carbons. Finally, a 7.3 wt% share belonged to the iso- and ante-iso- isomers⁶. That is in line with the results reported by Haas and Taylor [130] and Vetter and Wegner

⁶ iso such as isopalmitic when the branch is located on penultimate carbon from end of the chain, and ante-iso such as ante-isopalmitic when the branch is located on 2 but last carbon from end of the chain

[131]. The former [130] claimed that, the majority of isomers had the branch position on C7-C13 for isostearic acid. In addition, Cason and Winans [132] uncovered a 30-48 °C fall in the melting point when the position of the methyl group is on the 8-14th carbon of the methyloctadecanoic acid isomers. These results together highlight how the selectively of the microporous solid acids H-Ferrierite could influence suppressing melting point (in the saturated form) by the production of the most suitable isomers.

Wiedmann et al. [123] investigated the performance of five different commercial ferrierites. The yields towards isomerization at the 88 wt% conversion from highest to the lowest were detected to be H-Ferrierite-amm -107, H-Ferrierite-10, H-Ferrierite-amm-8.5, H-Ferrierite-K-8.5, H-Ferrierite-amm-27.

In summary, H-Ferrierite-amm-10, H-Ferrierite-K-9, H-Ferrierite-amm-8.5, H-Ferrierite-amm-27.5, H-Ferrierite-10 had the most significant performance towards the isomerization of oleic acid. Table 2 highlights the best results from different ferrierites that were collected by this review.

Ferrirrite type	Manufacturer/Code	Yield of isomers (%wt)	Ref.
H-Ferramm-10	CP914C	87	[114]
Ferr-K-9	(HSZ 720KOA) Tosoh	84	[115]
H-Ferr-K-9	(HSZ 720KOA) Tosoh	83	[113]
H-ferr-amm-27.5	CP914	79	[110]
H-Ferr-10	HSZ722HOA(Protonated from)	62	[123]
H-Ferr-amm-8,5	CP7145	60	[123]
Ferr-amm-10	CP914C	42	[110]

Table 2. list of ferrierites based on yield towards isomerized products

1.5.1.3 Mordenite

Mordenite type zeolites have the general formula |Na₈(H₂O)₂₄|[Al₈Si₄₀O₉₆]-MOR. They have 8 and 12 ellipsoid shape membered ring channels and their structure is considered as 2-dimensional [127].

⁷ H-Ferrierite is referred to the commercial ferrierite available already in the protonated form.

In 1997, Hodgson et al. [122] and Tomifuji et al. [106] disclosed the isomerization of oleic acid using zeolites and more specifically mordenite-type zeolites.

Tomifuji et al. [106], demonstrated the effect of water presence as cocatalyst. Increasing the water/catalyst from 1 wt% to 2 wt%, at 280 °C (6h reaction time under N_2) led to increase of yield from 62 wt% to 77 wt%.

Ngo and Foglia [111] showed the effect of poisoning of the catalyst surface by triphenylphosphine and obtained the highest yield 78 wt% for mordenite-type zeolites at 280 °C after a 6h reaction time under N_2 .

Zhang et al. [108] examined the effect of impregnation of mordenite with platinum for the isomerization of oleic acid. Pt-H-Mordenite-amm-20 was used as the catalyst at 280 °C, after 5h under N₂ atmosphere plus 4h under H₂ to give a 64 wt% yield. Hence, this result suggests that the utilization of noble metals on the mordenite surface for isomerization of long-chain UFAs may not be reasonable.

Reusability experiments on mordenite, however, did not show suitable results [122]. To investigate that, H-Mord-Na-17,5 was used as the catalyst at 250 °C after 4h reaction time, under N₂ atmosphere and gave a 54 wt% yield. Using the same catalyst for a second run with the same conditions the yield of isomers dropped the yield to 41 wt%.

The catalyst/feed ratio was evaluated by Hodgson et al. [107] for the isomerization of oleic acid by H-Mordenite-Na-17 at 250 °C, for 4 h using three different loading configurations. Figure 10 shows that the yield of isomers rose from 26 wt% to 49 wt% when changing the ratio from 1.3 wt% to 2.5 wt%. However, from 2.5 wt% to 5 wt%, the yield reached 54 wt%, suggesting that, up to a certain level, enhancing the catalyst/feed ratio can make a significant change in the output of the run.



Figure 10. Effect of catalyst-to-feed ratio on the yield of isostearic acid [107]

Table 3 depicts the best results from different modernites that were collected by this review.

Mordenite type	Manufacturer/Code	Yield of isomers	Ref.
H-Mordenite-9,5	HSZ640HOA	78	[111]
H-Mordenite-7,5	HSZ620HOA	75	[106]
H-Mord-Na-7	CBV10A	70	[122]
H-Mordenite-9,5	HSZ620HOA	66	[106]
Pt-H-mordenite-amm-			[108]
20	NM	64	
H-Mordenite-120	HSZ690HOA	61	[106]
H-Mord-Na-17,5	CBV30A	54	[122]
H-Mord-Na-10	CBV20A	31	[122]
Mordenite-Na-10	(CP 500C-11)	<10	[108]
H-Mordenite-amm-10	(CP 500C-11)	<10	[108]

Table 3. List of mordenite zeolites ordered from having the highest to the lowest performance

1.5.1.4 Beta type zeolites

Beta type zeolites have a general formula such as $|Na_7|[Al_7Si_{57}O_{128}]$ -*BEA. They have 12-membered rings and have been recognized as a zeolite with 3-dimensional channel structure [127]. For this catalyst, considerable yields have been reported, however, compared to ferrierite and mordenite, longer reaction times were needed.

Zhang et al. [108] used beta type-zeolite for the isomerization of OA. Reaction time was an important factor for H-beta-25. A 7% yield improvement (from 25 wt% to 32 wt%) was obtained adding 2 h at 250 °C, while a 22 wt% improvement (up to 54 wt%) when extending the reaction time two more hours. Hence, the yield toward isomers did not seem to have a linear relationship with the reaction time. The acidity role was then validated using H-beta-50 in the same conditions. Increasing Si/Al, which lowers the acidity, increased the yield from 54 wt% to 59 wt%. After that, the yield toward isomers enhanced to 62 wt% by eu⁺³ ion exchanging of the same catalyst under the same conditions. The authors also illustrated the effect of the feedstock carbon chain length by using a 22-carbon unsaturated fatty acid the erucic acid. H-beta-50 zeolite significantly improved the yield from 59 wt% for OA up to 78 wt% for erucic acid. They also carried out a continuous experiment using H-Beta-50 at 250 °C with a 2ml/h flow of OA on a fixed bed reactor. The yield was 49 wt% at this condition and with increasing the flow rate from 2 to 6 ml/h, the yield dropped to 23 wt%. Platinum and palladium were loaded on H-Beta-50 in this patent [108] with N_2/H_2 as atmosphere. Pt-H-Beta-50 at 250 °C after 7h provided 55 wt% yield, which is 4 wt% lower than the H-Beta-50. Nevertheless, Pt-H-Beta-50 had the highest yield (73 wt% after 14 h) under a 3 bar nitrogen atmosphere after which it was exposed for 6h under a 32 bar hydrogen. The addition of 32 bar of hydrogen added just 1 wt% to the final yield, producing 10 wt% of cracked products as consequence. Therefore, the addition of hydrogen at high pressures for Pt-loaded beta zeolite did not show a considerable influence. Pd-H-Beta-50 however, demonstrated the same yield of 73 wt% at higher temperature (280 °C) and for shorter reaction time (5h under nitrogen and 5 h under hydrogen). Acceptable yields by beta type zeolite were associated with having strong acidic sites, suitable acidic density as well as accessible channels for LCUFAs.

Zhang et al. [133] converted the ester form of oleic acid to its branched forms via H-Beta-27 at much lower reaction times as compared to H-Beta-50 [108]. A 66 wt% yield was obtained at 250 °C and 2 h of reaction time in a batch stirred reactor under a nitrogen atmosphere. This result uncovers the superiority of H-beta-27 over H-Beta-50 and H-Beta-25 in terms of reaction time. Zhang et al. [133] showed the positive effect of water as co-catalyst since a 10 wt% water/feed increased the yield of BMOs from 28 wt% to 40 wt% at 250 °C (for 5 h) when using H-Beta-25. However, the result of the isomerization experiments on OA and MO using H-Beta-360, showed that best yields could be obtained when there was no water as co-catalyst [49]. Reaume and Ellis also demonstrated that isomerization of fatty acids rather than their ester forms can end up with higher isomer yields when using H-Beta-360 zeolite (a 50 wt% isomer yield was obtained when fatty acids were used vs. 40 wt% isomer yield when fatty acid methyl esters were used).

Reaume and Ellis [112] investigated the isomerization of a different combination of SFAs and UFAs through a 6 h isomerization under H-beta-amm-12.5 at 260 °C followed by a 16 h hydroizomerization under 0.5 wt%Pt-beta-amm-12.58 at 300 °C. The yield towards 16⁺ carbon chain fatty acids ranged from 9 to 40 wt%. The highest yield was attained when the feed contained the highest amount of polyunsaturated fatty acids (54 wt%) whereas, the lowest yield was attained when the feed contained the highest amount of saturated fatty acids (92 wt%). However, since the majority of isomers were unsaturated, they were prone to undergo geometrical isomerization known as cis- to trans- isomerization. As a result of the deteriorating effect of trans isomers, skeletal isomerization effect on CFP was overwhelmed and the cloud point of the final product had a 4.4 °C increase. Long reaction times results can be a weak point for H-beta-amm-12.5 zeolite. The experiments of Sarker et al. [115] showed the effect of catalyst surface poisoner (TPP) on H-beta-amm-12.5 at 280 °C and different reaction times 4-24 h. The addition of 1.6 wt% TPP/catalyst was effective in increasing the yield to 73 wt% though at 24 h reaction time. Table 4 demonstrates the best results from different beta zeolites that were collected by this review.

Table 4. list of beta zeolites on the basis of Yield towards isomerized products in terms of zeolites

Beta type	Yield of isomers (wt%)	Ref.
Pt-H-beta-amm-50	74	[108]

⁸.5wt% presents the weight percent of platinium on zeolite surface

H-beta-amm-12.5	73	[115]
Pd-H-beta-amm-50	73	[108]
H-beta-27	66	[124]
CU ⁺² -H-beta-25	65	[124]
Eu ⁺³ -Hbeta-50	62	[108]
H-beta-25	54	[108]
H-beta-360	50	[49]
H-beta-12.5	50	[112]

1.5.1.5 ZSM-5

ZSM-5 zeolite has been widely used so far for cracking processes in the petrochemical industry although not as much for the isomerization of LCUFAs. H-ZSM5amm zeolite has the general formula $|Na_n(H_2O)_{16}|[Al_nSi_{96^-n}O_{192}]$ -MFI and it has been recognized as a 3-dimensional channel structure zeolite that owns 10 membered-ring channels [127]. To the best of our knowledge, the only research on the isomerization of LCUSFAs was done by [115]. They used a H-ZSM5-amm-11.5 catalyst at 260 °C, for 24 h, combined with 2 wt% TPP/cat as the co-catalyst, and 9 bar initial pressure of argon to obtain 84 wt% yield of branched methyl stearates after hydrogenation and esterification. This result, despite having a 24 h long reaction time, showed a great potential for the isomerization of LCUFAs for further research.

1.5.1.6 H-MAS-5

H-MAS-5 is a beta type zeolite with larger pores which is also is known as mesoporous beta zeolite. Zhang et al. [134] concluded that H-MAS-5 has a higher acid site's density as compared to H-Beta as well as better accessibility compared to H-Beta when it comes to LCUFAs. Larger pores of 25 Å account for this superiority. Zhang et al. [134] suggested that the pore size is the most critical factor when comparing the activity of different Beta type zeolites for isomerization of fatty acids. Although, Zhang et al. [109] obtained just 37 wt% yield toward iso-oleics from OA at 250 °C, after 5 h, and under 3.4 bars of N₂ (initial pressure) as reaction atmosphere.

1.5.1.7 Omega zeolite, L, Y

Other than 5 the previous zeolites with their different structures, 2 other 1dimensional and another 1-dimensional has been studied in different patents [106], [108], [122]. Zeolites such as L(1-dimensional), Y(3-dimensional), and omega(1dimensional) were tested for the isomerization of oleic acid. Notwithstanding, and apart from H-L-10 they were not as effective as previously mentioned zeolites. The highest yield by the mentioned catalyst when operated at 250 °C for 4 h was 52 wt%.

A detailed study by Hodgson et al. [122] showed that a factor defined as (max crystalline diameter, L)/(max crystalline diameter, D) played an extremely important role in 1-dimensional zeolites such as L or mordenite. In various experiments, it was confirmed that having a L/D higher than 10 and a Si/Al of 10 provided the best results (almost 50 percent yields towards isostearic acids). For a L/D less than 10, the IA yields were not more than 9 %.

In conclusion for LCUFAs, the zeolites could be prioritized as ferrierite> mordenite> Beta> ZSM-5> L, based on Table 1 and abovementioned results. According to what was concluded by the authors, the best results belong to ferrierite having 2 dimensional as well as 8- and 10-membered ring structure. Then, mordenite having 1-dimensional as well as 8- and 12-membered ring structures. Next, beta having a 3-dimensional as well as 12-membered ring structure. It is of interest to note that Si/Al ratio for ferrierite and mordenite is in the same range (10 and 9.5 respectively) and for beta is much more (50). In addition, water has been proved to be a good co-catalyst for ferrierite and mordenite whereas there are still doubts for beta.

1.5.2 Isomerization of LCAs by zeolites

The aim of this part is to extract the knowledge on the most recent catalysts used for isomerization of long-chain alkanes (LCAs) as well as the latest knowledge on the effective parameters for the isomerization of LCAs. Then by further interpretations and with these data feed the research on isomerization of LCSFAs.

The history of isomerization of alkanes goes back to the 1940s, when the first commercial plant was established to produce isobutane from butane in 1941 [63], [96]. Long linear chain hydrocarbons having more than 16 carbons have been generating a

considerable interest from oil refining to diesel fuel production because of their growing availability [135]. The role of isomerization in this context is to promote the reduction of the freezing point of this range of hydrocarbons. For instance, the freezing point of hexadecane is 18 °C whereas, the freezing point of 2-methyl pentadecane (branched hexadecane on the second carbon by a methyl group), and 5-methyl pentadecane are - 10 and -31 °C respectively [16][136]. There has been extensive research, to set the stage to utilize these compounds as fuel or other added-value chemicals via isomerization. The majority of the research has been focused on micro/mesoporous solid acid catalytic processes [44].

Hydroizomerization of saturated long-chain hydrocarbons by solid acids has been reviewed by several publications [135], [137]–[139]. However, the most recent results have been condensed in the reviews of Mäki-Arvela et al. [44], Zschiesche et al. [140] and Aitani et al. [95]. Catalysts and their yields have been organized in Table 5 based on the highest to lowest yield toward isomers.

	WHSV (h ⁻¹)	H ₂ /Fee	Catalyst	Si/Al	T (°C)	Р	Yi	Ref.
Feed		d(mola				(bar)		
		r)						
n-C ₁₆	1.1	10.9	Ba5wt%Pt-ZSM-12	60	295	60	80	[141]
n-C ₁₆	2-100	20	α-Al ₂ O ₃ -1wt%Pt-H-	11	220	30	80	[142]
			Beta					
n-C ₁₆	2-100	20	1wt%Pt-H-Beta	26	220	30	76	[143]
n-C ₁₆	1	6	.6wt%Pt-ZSM-23	60	270	30	74	[144]
n-C ₁₆	2-100	20	.86wt%Pt-Beta-Na	15	220	30	73	[145]
n-C ₁₆	3	4	.2wt%Pt-Al-MCM-48	5	240	20	70	[146]
			.4wt%Pt-Al-MCM-48					
			(the same result for					
			pt loadings)					

Table 5. Catalysts and their yields based on yields towards isomers for LCAs

n-C ₁₆	3	4	.3wt%Pt-HY-30A	24.8	240	20	53	[146]
n-C16	1	1000	0.5wt%Pt-ZSM-22	100	296	40	49	[147]
n-C ₁₆	2.5 min	600(vol	.3wt%Pt-ZSM-23	100	300	40	48	[148]
		%)						
n-C ₁₆	2-100	20	.93wtPt-H-Beta	15	220	30	44	[145]
n-C ₁₆	3	4	.3wt%Pt-HY	24.8	240	20	43	[146]
n-C ₁₆	Batch 2h	-	.5wt%Pt-Al-MCM-41	20	350	103(H ₂)	40	[149]
			Cat/Feed 1 wt%					
n-C ₁₆	1.3	500	γ-Al ₂ O ₃ 3wt%Pt-H-	150	290	75	36	[45]
		(vol%)	Beta (80wt%beta)					
C15-	LHSV	30	.5wt%Pt-HY	100	310	34	34	[150]
C18	1h ⁻¹							
n-C ₁₆	Batch 2h	-	.5wt%Pt-Y	2.5	350	103(H ₂)	30	[149]
			Cat/Feed 1 wt%					
n-C ₁₆	1.4	600	.3wt%Pt-ZSM-23	50	270	40	29	[64]
C15-	LHSV	30	.5wt%Pt-HY	5.5	310	34	23	[150]
C18	1h ⁻¹							
n-C ₁₆	Batch 2h	-	.5wt%Pt/H-Beta	50	350	103(H ₂)	22	[149]
			Cat/Feed 1 wt%					
n-C ₁₆	1.3	500	.3wt%Pt-γ-Al ₂ O ₃ –H-	150	290	75	18	[45]
		(vol%)	Beta (50wt%beta)					
n-C ₁₆	Batch 2h	-	.5wt%PtZSM-22	63	350	103(H ₂)	13	[149]
			Cat/Feed 1 wt%					
n-C ₁₆	1.3	500	.3wt%Pt-γ-Al ₂ O ₃ –H-	150	290	75	7	[45]
		(vol%)	Beta (20wt%beta)					
n-C ₁₆	Batch 2h	-	.5wt%Pt/ZSM-5	35	350	103(H ₂)	6	[149]
			Cat/Feed 1 wt%					
1		1						

Among the investigated catalysts in Table 5, Pt-H-ZSM12-60, Pt-Alumina-Hbeta-11, Pt-H-Beta-26, Pt-H-ZSM-23-60, Na-exchanged Pt-H-Beta-15, and Pt-Al-MCM-48-5 resulted in the highest yields of iso-hexadecanes from hexadecane. It should be noted that the majority of results have been obtained in fixed bed continuous systems unlike what was reviewed for the isomerization of LCUFAs. In continue, the crucial parameters for isomerization of LCAs will be discussed.

The effect of ion-exchange of zeolites on the isomerization yield has been widely investigated in the case of LCAs conversion. For instance, Liu et al. [151] exchanged sodium with alkaline earth metals (Mg, Ca, Ba, Sr) in H-Beta-Na-15.5 and they increased the conversion yields from 51 wt% to 67 wt%. They even achieved 95.4 % selectivity toward isomers following on exchange with Ba.

The Si/Al ratio affects the acidity of zeolites also with remarkable effects on the conversion yields toward isomers. The higher the ratio, the less the acidity and the latter is the parameter that could lead the reaction in the desired path, which is branching or even undesired one such as cracking [32],[152],[153][44]. Therefore, selecting the zeolites it is crucial to pay attention to the Si/Al ratio. In this regard, some of the works have tailored the acidity by advanced methods. These methods are summarized in Table 6. However, zeolites having Brønsted acid sites do not always show significant isomerization performance. Depending on the operating condition, HDO could be stimulated via hydrogenation-dehydrogenation reactions. Cracking and rapid deactivation via coking might be another side-reaction promoted by these acidic sites [128] [129]

The balance between metal dispersion on the surface and the acidity of the catalyst plays an extremely important role in the isomerization of linear alkanes. In this case, novel methods are used to decrease the acidity and to tune the acidity with metallic sites. When there is a suitable balance, dehydrogenation is performed by the first metal site. Then the acid sites are strong enough (neither too strong nor weak) to produce the carbocation and branch the dehydrogenated molecule with the lowest possibility of generating cracking reactions. Finally, the appropriate dispersion of metal paves the way for hydrogenation and completing the reaction [153] [44]. This factor is so important that it was concluded by Batalha et al. [143] to be more dominant than temperature and the effects of pressure. Batalha et al. [62] revealed that this balance

can be determined by thenmetallic sites /protonic sites ratio measured by ammonium heat of adsorption.

Impregnation also plays a major role for the performances of the catalysts designed for the isomerization. It has been suggested by Martins et al. [154] that loading platinum through ion-exchange on zeolite ends up with better results when compared to impregnation. They discovered that, after impregnation, the platinum nanoparticles are introduced to the zeolite surface as large agglomerates. Whilst, when using ion exchange, the nanoparticles are introduced also inside pores and channels, in addition to the surface loading. The distribution of metal has also been studied by [155] via two different impregnation methods. The SAPO-11 Pt loading was carried out by incipient wetness and colloidal impregnation. The result showed that after incipient wetness, the metal particles were located close to the entrance of the pores. Whereas, after colloidal impregnation, the metal particles were dispersed on the external surface. However, from a reducibility point of view, the wet incipient was expressed in another study, as the superior loading method [156].

The influence of precursor is of importance on size, location, and dispersion of the Pt nanoparticle on the zeolite surface. In [147] the authors analyzed the effect of impregnation with different platinum precursors such as Pt(NO₃)₂, H₂- PtCl₆, and Pt(NH₃)₄Cl₂. They concluded that precursors with platinum with the valence state of Pt(IV) favored the promotion of small nanoparticles. In addition, the Pt in anionic position resulted in improved dispersion and smaller sizes. Moreover, precursors with chlorine that did not include amine groups, dispersed the platinum more effectively owing to a lack of ammonia reduction after the post-calcination process.

Stability is essential for a catalyst to be exploited in industrial applications. In the n-dodecane isomerization study, (Niu et al. [157] reported a 204 h stability for the isomerization of n-hexadecane using 2wt%Pt-ZSM-22.

The available sources on isomerization of LCAs also provide more details of the relationship between pressure, temperature, and chain length with isomerization yield. Kinetic studies on alkanes suggest that higher pressures, lower temperatures, and shorter chains favors the isomerization rather than cracking [158] [159].

The effect of process mode between batch and continuous on the isomerization yield is extremely important. As an example, for the isomerization of n-hexadecane over 0.5 wt %Pt-SAPO-11 Park and co-workers [149] reached a 38 wt% conversion at 350 °C after a 14 h reaction time under 103 bar H₂. While Du et al. [160] reported an almost complete conversion of n-hexadecane reaching 96 wt% at 325 °C, 1 h⁻¹ WHSV, and 60 bar H₂. In other words, they achieved better results at much milder conditions. Superior distribution of hydrogen on the zeolite surface in continuous systems compared to batch ones justifies the better performance of continuous systems even in milder conditions and lower residence times [44].

1.5.2.1 Techniques for modification of catalyst structure in the isomerization of alkanes

One of the major differences between the studies of isomerization on LCAs and LCUFAs is the complexity of zeolites that have been used for the isomerization of LCAs. The aim of the present review is to highlight the positive differences to be used in the isomerization of LCSFAs. As reported in Table 5, zeolites that have been recently used for the isomerization of LCAs have been structurally modified by different methods to enhance the process efficiency by increasing yields towards mono-branched isomers while minimizing coke formation. As such, a list of different approaches are reported in Table 6.

Ion exchange with cations (Ba ²⁺) to reduce acidity	[141]
Ion exchange with cations (Sr^{2+}) to reduce acidity	[151]
Ion exchange with cations (Mg^{2+}) to reduce acidity	[144]
Ion exchange with cations (Fe ³⁺) to enhance acidity	[161]
Solvent-free synthesis method to enhance acidity	[160]
Alumina coating to avoid typical zeolite agglomeration	[142]
Morphology conversion from needle shape to bundle shape	[162]

Table 6. Different techniques for modification of zeolites

Preparation of nanosheets	[163]
Synthesis of zeolite like materials (SAPO-11)	[160],[164],[156],[165]
Synthesis of zeolite like materials (ZSM-22)	[64], [147], [162], [166]– [168]
Synthesis of zeolite like materials (ZSM-35)	[64]
Synthesis of zeolite like materials (ZSM-48)	[64]
Synthesis of bimetallic bifunctional zeolites (Rh as promoter+Pt)	[169]
Hydro/dehydrogenating metal agents other than Pt (Pd)	[170]
Hydro/dehydrogenating metal agents other than Pt (Fe)	[171]
Hydro/dehydrogenating metal agents other than Pt (Ni)	[172]
Hydro/dehydrogenating metal agents other than Pt (Ni-Mo)	[173]
Hydro/dehydrogenating metal agents other than Pt (Ni-Cu)	[174]
Synthesis of hierarchical zeolites for enhancing the mass transfer by dual templating	[164],[162]
Synthesis of hierarchical zeolites for enhancing the mass transfer by desilication through alkali treatment	[168]
Synthesis of hierarchical zeolites for enhancing the mass transfer by dealumination through acid treatment	[164]
Synthesis of composite materials for enhancing the mass transfer intergrowth micro/mesoporous	[166]

In summary (for LCAs), the presence and exploitation of newer generations of zeolites have been highlighted. Catalysts such as Ba-.5 wt%Pt-ZSM-12, α -Al₂O₃-1 wt%Pt-H-Beta, 1 wt%Pt-H-Beta, 0.6wt%Pt-ZSM-23, 0.2 wt%Pt-Al-MCM-48 (as listed in Table 5) have shown high yields of isomerization. Therefore, one of the most important differences with isomerization of LCUFAs is that the catalysts for LCAs are more tailored as listed in Table 6. Another important difference is that LCAs have been mainly studied in continuous mode. However, some similarities can validate the relationships between the two topics. For LCAs, 1-dimensional catalysts have shown better performance than 3-dimensional ones which is in line with the results for LCUFAs. This result could validate the relationship between different but similar materials such as LUFAs and LCAs.

1.5.3 Isomerization of LCSFAs by zeolites

The history of bifunctional zeolites dates back to 1989 when Tsao [102] prepared zeolites with a metal dispersed surface [21]. Noble-metals were impregnated on different zeolite types; such as, ZSM-5, mordenite, and Beta. However, Kenneally et al. [21] were the first who utilized the bi-functional zeolites for the isomerization of saturated fatty acids. Table 7 shows the research on the isomerization of long-chain saturated fatty acids such as octadecanoic and hexadecanoic acid. Experiences on isomerization of long-chain saturated fatty acids were collected in Table 7.

Feed	Product	Catalyst & Cat./Feed (wt%)	Si/Al	Т (°С)	P (bar), H_2	(h)	Yield (wt%)	Ref.
PA	BPAs	0.5wt%Pt/HBeta		285	40		42	[112]
		reed	2.5			6		
Coconut	+BPAMEs	HBeta Fred 4		260,300	15, 40		9	[46]
oil		6.5wt%PtHBeta 6.5wt%PtHBeta Feed	2.5			2		
SA	BSAs	0.4wt%Pt/HBeta Feed	2.5	340	6.8		6	[175]

Table 7 Yields of isomers from SFAs

A 0.4 wt%Pt-H-Beta-amm-12.5 was used for the isomerization of octadecanoic acid by Kenneally et al. [175]. The best result was obtained at 340 °C, after 6h, and under 6.8 bar of H₂ with a 6 wt% yield toward isostearic acids. They also performed other experiments with other catalysts such as pt-sulfated zirconia, 5 wt% alumina, and 1 wt%pt-chloride alumina. In the case of mentioned catalysts, the isomerization hardly proceeded or did not proceed at all. It should be stated that pt-sulfated zirconia had an effective performance on the isomerization of n-heptane and n-hexadecane representing short and long chain alkanes [176]. Likewise, alumina and chloride alumina impregnated with platinum had been traditionally used for isomerization of short chain alkanes [177].

Reaume and Ellis [112] released the fatty acids from coconut oil with a preliminary hydrolysis step. Fatty acids were composed of 92 wt% SFAs and 8 wt% UFAs. The process

involved an isomerization step by H-Beta-amm-12.5 at 260 °C, after 6 h, under 15 bar of H_2 , followed by a hydroisomerization using 0.5 wt%Pt-H-Beta-amm-12.5 at 300 °C, after 16h, and under 40 bar of H_2 . The final yield toward C16 and longer chain fatty acids was 9 wt% which, due to similarities, is in line with the results from [175].

In another publication [112] the hydroisomerization of pure hexadecanoic acid was performed using 0.5 wt%Pt-H-Beta-amm-12.5 at 285 °C, after 16 h, and under 40 bar of H₂. Yield toward iso-hexadecanoic acids was reported to be 42 wt%. The reported yield is rather controversial though and there is no general agreement with previous studies with the same catalyst. The reason may originated from the fact that isomer spectrums in GC/MS are busier or noisier than the spectrum for the linear molecule causing difficulties to identify them [33]. However, the product yield in that work was quantified by calculating the peak area of the product based on the calibration curve generated for hexadecanoic acid by GC/MS. As such, this may result in considerable errors.

Van Schalkwyk et al. [178] investigated on effect of the carboxylic group on WO₃/SiO₂. They concluded that the carboxylic group induced deactivation for this catalyst. Therefore, it can be concluded that impact of carboxylic acid on slow kinetics is unquestionable.

In summary, it could be concluded that for the isomerization of LCSFAs, the use of 3-dimensional zeolites, as well as batch mode experiments, can account for low yields. 3-dimensional zeolites have shown inferior performance in comparison with 1-dimensional and 2-dimensional zeolites in the isomerization of LCUFAs and LCAs as reviewed above. Also, in literature, 3-dimensional zeolites have recognized them as the least selective zeolites for isomerization of alkanes [32]. Therefore, conclusions were made for improvement of the yields and reduction of reaction time in the isomerization of LCSFAs. It was concluded that in the future experiments, using a continuous system with a variety of choices of catalysts and cocatalysts from the previous parts could boost the results on isomerization of LCSFAs.

The type of feed is also important. As reviewed before, different studies examined the effect of feed choice between carboxylic acid and ester form on isomerization yield.

Apart from Foglia et al. [125], all the results of [49], [112], [126], [175], [179], generated superior results when the carboxylic acid form was used. The reason was explained by some as the steric hindrance of the methyl ester group [2], [48]. However, when it came to the isomerization of unsaturated-rich feedstock and although the yield towards skeletal isomers was still higher, the ones towards undesired diastereomers were higher, finally the use of the ester form provided better result when it came to cloud point reduction. Therefore, in the case of isomerization of unsaturated fatty acid sources, prior esterification step is preferred.

1.5.3.1 Molecule size VS. zeolite pore size

This last paragraph investigates the link between the molecular size of the reactant and the pore size in zeolite catalysts. From the experiments reported in the previous sections, this aspect has not been investigated by the authors. That seems essential to review some information about the molecule size of a model LCSFAs and pore openings of the various zeolites after reviewing the best zeolite structures and their pore openings. The pore opening defines if the reagents pass through the channels of the heterogeneous catalyst, diffuse partially, or get blocked completely for the diffusion towards the pores and channels. To provide more information on pore opening of each investigated catalyst, Table 8 has listed the pore openings of common catalysts in hydroizomerization of LCAs. Considering stearic acid as one of the most occurring fatty acids in vegetable oil and animal fat, the width and length of the molecule have been reported to be 2.5 and 24.5 Å respectively [19]. Figure 11 depicts the structure and dimensions of the stearic acid.



Figure 11. Dimensions of stearic acid. Gray, white, and red spheres represent carbon, hydrogen and oxygen atoms respectively. Drawn by online open source application written by Herman Bergwerf [180]

Zeolite type	Pore opening (Å=1 ⁻¹⁰ m)
Pt/ZSM-22 (TON-10 ⁹ -1D)	4.4×5.5
Pt/ZSM-23 (MTT-10-1D)	5.2 × 4.5
Pt/ZSM-35(FER-8-10-2D)	3.5 × 4.8, 4.2 × 5.4
Pt/ZSM-48(MRE-10-AD)	5.6 × 5.3
Pt/ZSM-12 (MTW-12-1D)	5.7 × 6.1
Pt/ZSM-5 (MFI-10-3D)	53×56.51×55
Pt/A1-MCM-41 (MOR-1D)	26
Pt/H-V (EAU-12)	74
Dr/II 0 (DEA 12 2D)	
PUT-D (DEA -12-3D)	5.0×0.5, 5.1×1.5
Pt/Mordenite (Mor-8,12-1D)	6.5×7.5
Ferrierite (Fer-8-10-2D)	3.5 x 4.8, 4.2 x 5.4

Table 8. Difference between pore structures	s [149], [181]–[183]
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From Table 8 it could be also concluded that zeolites with large and extra-large pores are the more suitable candidates for isomerization [44].

1.6 Conclusion

This chapter reviewed the isomerization of long-chain LCUFAs, SFAs, and alkanes by zeolites. Either from the number of researches or the reported yields that could be readily observed that for UFAs and HCs, the research in this field is quite mature. The isomer yields from LCUFAs and LCAs higher than 80 wt% confirm this claim. Despite that, research is still going on toward enhancing the selectivity and conversions of the present catalysts for the industrialization of LCUFAs isomerization as well as elevating the efficiency of industrial processes for LCAs isomerization. However, the yields towards the isomerized products, from LCSFAs such as palmitic and stearic acid suffer from low amounts in addition to long reaction times (such as 16 or 22 h). The results of this study

⁹ Ring structure

suggest that, although there is not a large number of investigations on LCFAs, it is possible to receive aid from other similar fields. Our study provides the encouragement for research towards the production of high-quality biodiesel and biobased products from more economic sustainable resources as long-chain saturated fatty acids. Finally, some potential shortfalls need to be considered. First, the higher melting points as compared to UFAs and long-chain alkanes makes it difficult for continuous processes on a fixed bed set ups. Second, SFAs do not have any double bonds in comparison with UFAs. Besides, they have a carboxylic group which is considered as a catalyst deactivator compared to linear alkanes. The present review chapter suggests that the policy makers should stimulate the production of biofuels and biobased chemicals based on lipid waste, such as animal fat and Palm oil Fatty Acids Distilled (PFAD). We hope that further tests will prove such, theory which could be a useful aid for stepping up a gear towards sustainability. Further experimental investigations are needed to discover the best sustainabile catalysts delivering high yields at short reaction times.

2 Materials and methods

The present work considered a wide variety of materials for experiments. This chapter describes them all and explains the strategies that have been adopted to prepare the required catalysts or analytes. Furthermore, procedures by which the experiments were carried out, and the products were collected, and analyzed will also be discussed. Therefore, after specifying the materials, the instruments such as the reactors, the analytical tools, as well as experimental steps from A to Z will be identified.

2.1 Chemical substances

Several materials were purchased to perform all the steps of this work. Table 9 lists the materials' name, their chemical formula, CAS number, and the company they were purchased from.

Material name	Chemical formula	CAS	Supplier
Palmitic/hexadecenoic acid	$C_{16}H_{32}O_2$	57-10-3	Sigma Aldrich
Methyl Palmitate	$C_{17}H_{34}O_2$	112-39-0	Sigma Aldrich
BSTFA (N,OBis(trimethylsilyl)trifluoroacetamide)	$C_8H_{18}F_3NOSi_2$	25561-30-2	Acros Organics
Pyridine	C_5H_5N	110-86-1	Sigma Aldrich
Ammonium Nitrate	NH ₄ NO ₃	6484-52	Sigma Aldrich
Iron (III) nitrate nanohydrate	$FeH_{18}N_{3}O_{18}$	7782-61-8	Sigma Aldrich
Tetraammineplatinum(II) dichloride	Pt (NH ₃) ₄ Cl ₂ ·xH ₂ O	108374-32-9	Sigma Aldrich
ZSM-5	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] xH2O$	70955-01-0	Zeolyst
Beta	SiO ₂ :Al ₂ O ₃	1318-02-1	Zeolyst
Acetone	C_3H_6O	67-64-1	Sigma Aldrich
Triphenilphosphine	$C_{18}H_{15}P$	603-35-0	Sigma Aldrich
Phenolphthalein	$C_{20}H_{14}O_4$	77-09-8	Sigma Aldrich
Glass microfiber filter (2.7 µm)	-	1823-070	Whatman
Distilled water	H ₂ O	-	RE-CORD
Hydrogen	H ₂	1333-74-0	Rivoira

Table 9. Materials and their specifications that were used in the experimental activities

Ethanol	C ₂ H ₅ OH	64-17-5	Sigma Aldrich
Potassium hydroxide	КОН	1310-58-3	Sigma Aldrich
Diethyl ether	$(C_2H_5)_2O$	60-29-7	Sigma Aldrich
Standard hydrochloric acid	HCl	7647-01-0	Sigma Aldrich



Figure 12. Materials that were used for the experimental activities

2.2 Catalyst preparation and characterization

2.2.1 Fe-H-ZSM-5

2.2.1.1 Grinding extrudates

Since the ZSM-5 was in the extrudate shape, it was ground to powder using a pestle and mortar (Figure 13).



Figure 13. extrudates were ground by a pestle and mortar

2.2.1.2 Conversion of Lewis ZSM-5 to Brønsted ZSM-5

In order to convert the catalyst to a Brønsted acid, which is essential for isomerization process, protonation is necessary. In the light of this, the recipe and the procedure of the preparation of 100 grams of HZSM-5 is presented below.

The Na-ZSM-5 zeolites was converted to H-form by three consecutive ionexchanges using calcinated Na-ZSM-5 (Figure 14) and an excess of 1 M aqueous NH_4NO_3 (Figure 15) with a solution/zeolite ratio of 10 ml/g at 80 °C for 1 hour (Figure 16). The resulting samples were dried at 105 °C (Figure 17) and calcinated again at 520 °C for 3 h (Figure 18).



Figure 14. Precalcination of the catalyst in the muffle furnace



Figure 15. Preparation of a 1 M solution of Ammonium Nitrate



Figure 16. Stirring ZSM-5 and Ammonium Nitrate for 1 hour at 80 °C



Figure 17. Filtration and drying at 105 °C



Figure 18. Final calcination at 520 °C and 3 hours

2.2.1.3 Impregnation

The impregnation of H-ZSM-5 was done by wet impregnation. For this step, 292 g Iron III nitrate nonahydrate was added and to 2100 ml isopropyl alcohol (Figure 19) and dissolved using an impeller at 100 rpm. Next, H-ZSM-5 was separated from Isopropyl alcohol at reduced pressure of 137 mbar and 40 °C (Figure 20).



Figure 19. Preparation of iron salt solution



Figure 20. Removal of the isopropyl alcohol under reduced pressure distillation

The precursor was then reduced under 130 mL min⁻¹ of hydrogen flow at 800 °C for 30 min. The catalyst changed the color (to black) after the reduction, which is a sign of a successful reduction (Figure 21).



Figure 21. Reduction of iron salt that was loaded on the H-ZSM-5

2.2.1.3.1 Simulation of catalyst distribution inside the reduction reactor

To ensure having a uniform catalyst bulk versus the hydrogen flow, an experiment was carried out with a quartz tube with the same inner diameter and length of the stainless-steel tubular reactor that was going to be used for the reduction process. The quartz tube was filled up with the catalyst powder with the same conditions as the stainless-steel reactor (Figure 22).



Figure 22. Preparing the identical dimension quartz tubular reactor filled up with catalyst powder

To simulate the process, the inlet of the quartz-sealed tube was connected to the hydrogen source. Then, flowrate of hydrogen was set at 130 mL min⁻¹. After the hydrogen flow started, it was observed that the catalyst was pushed along the reactor by the positive pressure of the hydrogen flow, and it took about one minute to get stabilized. At the end, the catalyst was compressed to the right side. As the result of this compression, a void area with the length of 5 cm length was created on the left side of the fixed bed (Figure 23).



Figure 23. Catalyst distribution during the simulation

Finally, the hydrogen line was purged and the catalyst was observed to have a discontinuous distribution (Figure 24).



Figure 24. Catalyst distribution after the hydrogen flows interrupted

The result of this experiment showed that with the targeted defined hydrogen flow-rate, the catalyst powder was compressed but this compression did not block the hydrogen flow through the catalyst. Moreover, the flowrate was high enough to prevent a channeling phenomenon.

2.2.2 Pt-H-beta

Beta zeolite (with its acid sites in Lewis form) was calcined at 550 °C for 12 hours to ensure that it was converted to its protonated from. Then, the Pt salt (Tetraammineplatinum (II) dichloride) was dried and added to the distilled water with a 2.1 (g water)/ (g zeolite) ratio for incipient wetness method. After preparation of the platinum salt solution, it was added drop wise to the zeolite powder. The solid was then dried at 65 °C for 48 h and then burned at 500 °C for 3 h. Eventually, it was transferred to a tubular reactor with Swagelok fittings equipped with $\frac{1}{2}$ " tubes at the beginning and at the end of the reactor as gas inlet/outlet (Figure 25).



Figure 25. Reactor scheme for the reduction step

Next, reactor the was inserted inside a tubular furnace. The reactor was purged for 5 min by nitrogen flow after which the flow was changed to hydrogen. With a heating rate of 5 °C min⁻¹, reactor was first heated to 120 °C and maintained at this temperature for 1 h to avoid zeolite steaming. The temperature was then raised and with the same heating rate to 320 °C and was kept for 1 hour at 320 °C to prevent overheating due to the combustion of ammonia. Finally, still using the previously-mentioned heating rate, the temperature of the reactor was raised to 500 °C for three hours under 130 mL min⁻¹. The reactor was then cooled under hydrogen flow down to the ambient temperature.



Figure 26. Catalyst during the treatment

2.2.2.1 Characterization of the catalyst

2.2.2.1.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was used to validate the claimed structure of the commercial support (beta zeolite from Zeolyst). SEM ZEISS Supra 40 combined with a field emission gun was used along with an Everhart-Thornley secondary electron detector to discover the morphology of the mentioned zeolite.

2.2.2.1.2 Physical adsorption (N₂ adsorption)

N₂ adsorption isotherms (BET) were calculated in a Quantachrome NOVA 2200E instrument in order to obtain the surface area and to compare the results with the claimed surface area by the support (beta zeolite) manufacturer company. First, 60 mg sample was dried at 200 °C for 48 h. Second, degassing was performed and measurements were carried out subsequently (200 °C for 24 h). [184]

2.2.2.1.3 X-Ray Diffraction (XRD)

A Cu Kα radiation was exploited to register the patterns of X-Ray diffraction (XRD). Catalyst sample was prepared and the analysis was carried out on a Rigaku Smartlab Cusource powder diffractometer. Power was set at 45 kV and 200 mA along with utilization of the Cu Kα radiation. Rate of scanning was fixed at two degrees per minute .02 degrees was programmed as the steps. A database known as Pearson's Crystal database was exploited for comparison of the results with the claimed morphology claimed by the manufacturer of the catalyst support.

2.2.2.1.4 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was performed on a fresh sample pf the catalyst by a macro TGA (LECO TGA 701) instruments. 10 L/min nitrogen flow was set and the heating rate of was fixed at 5 °C/min, maintaining three 1-h thermal plateau at 105 °C, 320 °C, and 500 °C. 1 \pm 0.1 g of the catalyst powder was loaded in a large TGA crucibles from ceramic with volume of 20 ml.

2.3 Instruments and methods

2.3.1 Micro-Reactor Test-Bench set-up and experimental procedure

MRTB or Micro Reactor Test-Bench (Figure 28) is an experimental set-up that was used for the preliminary hydrodimerization experiments. The MRTB system is composed of the following parts:

- Micro-reactor (described in section 2.3.1.1 below)
- Nitrogen cylinder (for purging).
- Argon cylinder with a max pressure of 200 bar, for leakage tests.
- Barrel filled with distilled water at 20 °C to quench the tubular reactor.
- Other utilities to obtain gases such as He, H₂, etc.
- An electric motor to create a reciprocal reactor moving during the experiments for a better mixing of the material during the reaction.
- Heaters
- Sand bath
- Valves for loading and releasing the gasses
- Compressed air line to flow and heat up the air through the sand
- Different temperature and pressure sensors for controlling purposes

2.3.1.1 Micro-reactor

The reactor is a 300 mm-long AISI 316 $\frac{3}{4}$ -inch tube (outer diameter), modified with Swagelok fittings. It is equipped with a PT100, a 3-wire RTD temperature sensor (1/10 DIN accuracy class), a pressure transducer and a pressure relief valve for safety depressurization. The reactor is composed of three parts as shown in Figure 27: The top, the bottom and the tube. Its volume is 42 cm³. The maximum allowable pressure for the reactor is 319 bar at 400 °C.



Figure 27. Experimental reactor for preliminary experiments: a) Top; b) Bottom; c) Reactor complete.

2.3.1.2 The sand bed

The sand bath, is an air-fluidized sand bed system (FSB-4 Omega Engineering). The sand is heated by hot air flow already heated by 4 resistors. The mentioned system can rise the temperature of the sand to a maximum temperature of 540 °C. Every resistor, called Low, Medium, High and Boost, uses 1 kW of power, for a maximum of 4 kW when all resistors are turned on. However, to avoid resistors overheating (with consequent damage), they must not be operated at their maximum capacity. The entire system has a voltage of 240 V.



Figure 28. Micro Reactor Test-Bench at RE-CORD.

The sand bed of the MRTB is fluidized by means of compressed air at 0.2 bar, with a 68 l/min flow and the latter is always kept on to avoid the resistors overheating.

Sand temperature, pressure and temperature inside the reactor are continuously monitored by means of a National Instrument Data Acquisition System (NI-DAQ). It monitors and saves any data that the sensors collect. Three sensors are present to capture data: two temperature sensors (both PT100, 3-wire RTD temperature sensor, B accuracy class), one located in the bottom of the fluid sand bed and an external one (that is immersed to measure the temperature near the surface), and the third sensor is the one inside the reactor to monitor the progression of reaction. The scheme of the MRTB system is shown in Figure 29.



Figure 29: Micro Reactor Test-Bench (MRTB) scheme[185].

2.3.1.3 MRTB Experimental procedure

For every experiment, the catalyst was dried at 105 °C and was added to the tubular reactor along with the feed at desired amounts (that were previously) defined. After closing the reactor, the whole unit was weighed. To ensure that the reactor was sealed, a leak test was done by injecting argon at 80 bar. If no leakage was detected, the reactor was then depressurized and purged 3 times with nitrogen at 5 bar. Afterwards, for the hydroisomerization reactions, an initial pressure of 5 bar of hydrogen was introduced to the reactor at the ambient temperature. In case of isomerization reactions, at this step, and instead of hydrogen injection, 5 bar of nitrogen was introduced as the initial pressure and the gas atmosphere of the reactor. Afterwards, by immerging the reactor in the hot fluidized sand bed, the reactor was heated at a high heating rate (120 °C/min) until reaching the temperature set point. The reaction start was considered when temperature of the reactor was at 95 % of the setpoint. Pressure and temperature data were monitored and recorded using LabVIEW computer program
[186] (Figure 33). Finally, the reaction was terminated by quenching using the tank filled with water at ambient temperature. The reactor was then kept in the quenching tank for 20 min. The reactor was then weighed after depressurization after which all the material was transferred to a beaker.

2.3.2 Parr Engineering Autoclave set-up and experimental procedure

For the hydroisomerization experiments with Pt-H-beta catalyst, an Autoclave Engineering Parr 4564 stirred reactor was used (Figure 30). This set-up is composed of four major parts (Figure 31) as follows:

- The reactor vessel equipped with pressure manometer, J type thermocouple, and valves for liquid sampling, gas discharge and release. A rupture disc is embodied in the cap of the vessel so that at pressures higher than 207 bar the rupture disc bursts and releases the pressure of the vessel. This is to protect the whole vessel to break into pieces under very high pressures.
- Stirring system (stirring up to 700 round per minute)
- A 4842 Parr controller for temperature regulation
- A 700-W ceramic heater for heating the internal temperature of the reactor vessel to the desired set point (up to 350 °C)

Maximum allowable pressure for this set-up is 207 bar at 350 $^\circ \text{C}.$



Figure 30. Autoclave Parr 4564 set-up inside the fume cupboard during an experiment



Figure 31. Different part of the autoclave set-up

2.3.2.1 Flow regime with the desired loading

An experiment was carried out to ensure adequate stirring inside the autoclave. Since the volume of the utilized autoclave was 160 ml and it was intended to be loaded with low amounts (less than one-third of its capacity), a simple plastic jar was cut with the dimensions of the bottom cylinder of the autoclave. Then it was loaded with 35 g water and 20 g zeolite powder and well-mixed to simulate the mixture of zeolite-palmitic acid during reaction time. Water was chosen instead of palmitic acid because at the ambient temperature palmitic acid is solid and doing such an observation would not be possible. Finally, the stirrer was set at 600 rpm and the simulation set-up was monitored. This experimental simulation showed that the quantities of feed and catalyst that were going to be employed inside the autoclave were enough to have an effective stirring (Figure 32).



Figure 32. An experiment to ensure well-performed stirring

2.3.2.2 Parr autoclave experimental procedure

For every experiment, the catalyst was dried at 105 °C and was added to the autoclave along with the feed at previously defined conditions. After closing the reactor, the whole system was weighed. To ensure that the reactor was sealed, a leak test was performed by injecting hydrogen at 50 bar. If there was not any leakage, the reactor was then depressurized and purged 3 times with hydrogen at 5 bar. Subsequently, an initial pressure of 15 bar was imposed to the reactor at the ambient temperature. Afterwards, the reactor was heated with a 11 °C/min heating rate until the temperature set point after which the stirrer was set to 600 rpm. For every experiment, the pressure was raised to the desired experimental pressure when the temperature reached at 250 °C by injecting the hydrogen. The reaction start time was considered when temperature of the autoclave was at 95% of the setpoint. Pressure and temperature data were monitored and recorded using the LabVIEW software [186](Figure 33). Finally, the reaction was terminated by quenching the reactor in ice (Figure 34). The reactor was kept in the ice-water mixture for 20 min. The autoclave was weighed before depressurization, after which in some cases some experiments were performed to

analyze the gas. For this, gas bags were filled up by depressurizing the autoclave. The autoclave was weighed again after depressurizing after which it was opened and then all the material was transferred to a beaker.



Figure 33. Controlling and recording the process conditions by LabVIEW computer program [186]



Figure 34. Quenching the autoclave by ice and air cooler

2.3.3 Product collection

Either after experiments with the MRTB or the Parr autoclave, products were transferred into a beaker and weighed. Moreover, after the material was transferred, the reactors were washed by acetone and the washed part was added to the beaker.

2.3.3.1 Catalyst separation

Catalyst was separated by vacuum filtration and the system was composed of several different parts (suction pump, Erlenmeyer flask, funnel, and a filter with pore diameter of 2.7 μ m).

Since at the end of the experiments, the product was mixed with the heterogenous catalyst, and this mixture was often in a non-filterable solid state, the mixture was weighed and dissolved in acetone. The amount of acetone was calculated on the basis of the product weight. For instance, if the product was 30 g, then it was dissolved in 300 g of acetone. Therefore, after transferring the mixture to a beaker with a magnetic stirrer inside on a heating plate, the solution was heated while stirring so that all the solid material was dissolved in the solvent apart from the solid powder (catalyst). Subsequently, the content of the beaker was added little by little to the funnel covered by the filter. At the end, 50 ml of hot acetone were used to wash the solid residue.



Figure 35. Catalyst cake on the filter after solvent wash

2.3.3.2 Solvent removal

Solvent removal was done using a rotary evaporator IKA RV 10 control (Figure 36). For every experiment, the solution from the catalyst separation step (2.3.3.1) was transferred to a spherical flask and attached to the rotary evaporator instrument. The procedure for solvent removal was as described in Table 10:



Figure 36. Rotary evaporator that was used for the solvent removal

Steps	Time	Flask residual	Flask temperature	Flask rotation speed
	(min)	pressure (mbar)	(°C)	(rpm)
1	0-30	750	54	100
2	30-60	700	54	100
3	60-90	700	56	100
4	90-120	700	58	100
5	120-150	600	60	100

Table 10. Solvent removal procedure

It should be mentioned that after the first 120 min, the weight of the product was measured. At this point, if the amount of the product was more than expected (more than the collected material subtracted by catalyst that was collected after reaction mentioned at 2.3.3.1), the evaporation was continued at step 5. Otherwise, Rotary evaporation was interrupted at step 4.

2.3.4 Analytical methods

Different analytical methods were used to define the chemical composition and physical specifications of the products. gas chromatography with mass detector. Gas chromatography with flame ionization detector, gas analysis, acid value, and melting point analysis were the analytical techniques employed.

2.3.4.1 GC-MS & GC-FID

The aim was the chemical characterization and quantification of the sample using gas chromatography with flame ionization detector (FID) for the quantitative analysis and mass detector (MS) for the qualitative analysis.

2.3.4.1.1 Sample preparation

The sample was subjected to a derivatization reaction to form the corresponding trimethyl-silyl derivative using BSTFA (BiS TriFluoro Acetamide) as a silylation agents and pyridine as solvent. After dilution with iso-octane, the sample was injected in the GC/MS for the qualitative analysis and in the GC/FID system for the quantitative analysis in area %.

2.3.4.1.2 Instrument condition: GC/FID

The GC/FID analysis was done using a gas chromatograph Agilent 7890 with flame ionization detector (FID). The column used for the separation was a HP5 (5% phenyl – methylpolysiloxane), 30 m, 0.25 mm of internal diameter and 0.10 μ m film thickness. The analysis was performed in split mode at 270 °C with an oven gradient temperature from 50 °C to 320 °C.



Figure 37. GC-FID for quantitative analysis

2.3.4.1.3 Instrument condition: GC/MS

The GC/MS analysis was performed using a gas-chromatograph (Shimadzu GC 2010) equipped with a mass spectrometer detector (MS). The column used for the separation was a HP5 (5% phenyl – methylpolysiloxane), 30 m, 0.25 mm of internal diameter and 0.25 μ m film thickness.

The analysis was performed in split mode at 270 °C with an oven gradient temperature from 50 °C to 320 °C. The mass detector operated in electron impact mode at 70 eV with a mass range from 40 to 800 uma. The mass spectra were analyzed using the NIST library.



Figure 38. GC/MS for qualitative analysis

2.3.4.1.4 Quantitative and qualitative interpretations

The identification of the compounds was done by GC/MS analysis by comparison of the mass spectra with those present in the NIST library.

The quantification results were done by GC/FID analysis and were expressed as area %.

2.3.4.2 Acid Value

The measure of the acid value was performed by titration to understand the decarboxylation degree of the product as support for validating the gas chromatography results. To calculate the acid value the following steps were conducted:

2.3.4.2.1 base solution preparation (KOH)

1.40 g of Potassium Hydroxide was dissolved in 250 ml of Ethanol to produce a 0.1 N basic solution of KOH.

2.3.4.2.2 Solvent preparation:

Ethanol and Diethyl Ether were mixed in a 1:1 vol. to prepare the solvent for dissolving the solid/liquid samples.

2.3.4.2.3 Solvent neutralization

Three drops of phenolphthalein were added to the solvent and then titrated by the basic solution mentioned in section 2.3.4.2.1 until it changed color (to pink) to ensure having a neutral solution.

2.3.4.2.4 Defining the exact concentration of the base solution

10 ml of a 0.1 M standard hydrochloric acid and 50 ml of solvent from section 2.3.4.2.3 were mixed and titrated by the base from section 2.3.4.2.1 in triplicate. Subsequently, KOH was added until the solution changed color. The volume of consumed base gave the exact concentration of the basic solution from the equation(1) as follows:

$$N_1V_1 = N_2V_2$$
 (1)

Where

 N_1 is Normality of the hydrochloric acid (gmol/lit) V_1 Volume of the hydrochloric acid added to the Erlenmeyer flask (lit) N_2 is Normality of the basic solution (gmol/lit) V_2 Volume of the base consumed for titration (lit)

2.3.4.2.5 Analyte preparation

3 samples of the same product were prepared by addition of 0.2 g of the product dissolved in 100 ml of the solvent reported section 2.3.4.2.3 inside an Erlenmeyer flask.

2.3.4.2.6 Titration

The indicator was added to the sample solution. The base solution was then added until the sample was neutralized which was shown by the color changing to pink (Figure 39). The consumed volume of the base was recorded and calculated from equation (1)

Number of acidity =
$$\frac{V*N*56.1}{m}$$
 (mg KOH/g sample) (2)

where

N is the normality of the basic solution defined in 2.3.4.2.4 (mol/lit)

V is the volume of the consumed basic solution for titration (ml)

56.1 g/gmol is molecular weight of the KOH m Weighed sample described in section 2.3.4.2.5



Figure 39. Steps of titration for determining the number of acidity

2.3.4.3 Gas phase analysis

Gas phase analysis was performed using an Agilent 490 Micro-GC. At the end of the experiment, the autoclave was cooled down to the ambient temperature. Then, after opening the outlet valve of the autoclave and inlet valve of the gas-bag, noncondensable gases were transferred to the gas-bag (Figure 40).



Figure 40. Transferring non-condensable gasses from autoclave to the gas-bags

The gas transfer was done after autoclave cooling, in order to avoid condensable gases in the to the gas-bags. Later, the gas inside the gas-bags, was completely transferred to the Micro-GC. Two columns were used: The first one being a Molsieve for light gases (hydrogen, nitrogen and oxygen) and the second, a PoraPLOT U (PPU) was used for hydrocarbons (C1-C3). They worked at constant temperature (90 °C) so as the injector. The carrier gas was argon. Figure 41 depicts the gas flow diagram.



Figure 41. Gas flow diagram[187]

2.3.4.4 Melting point evaluation

The temperature at which a solid substance melts and becomes a liquid is the melting point.

One gram of the sample was transferred into a 2 ml dram vial. If the sample was solid at ambient temperature, the dram vial was heated using a warm water bath so that it turned to liquid state. At this point an already prepared capillary U shape tube (Figure 42) was inserted inside the warmed liquid. As a result, the tube absorbed the liquid (about one centimeter length of the tube). Then, the capillary U-tube was placed inside the freezer at -18 °C for almost 16 hours so that the sample could solidify inside the tube. After that, the U-tube was fixed inside a beaker containing an already subcooled brine water mixture and maintained by a stand and a clamp. The water was slowly heated by a heating plate while the temperature of the water was being monitored using a

thermometer. The temperature at which the sample started to slide down inside the tube was marked as the melting point. Different steps of melting point analysis are demonstrated in Figure 43.



Figure 42. Preparation of capillary U-shape tubes by flame



Figure 43. Step of melting point analysis: a) Clean dram vial b) loading with the sample c) Heating d) Freezing e) heating up on a hot plate f) Recording the temperature at which the sample slides down as melting point

3 Experimental designs

In this chapter, the series of trials that led to the production and optimization of hydroisomerization reaction using several catalysts will be explained. In the main part, the design of experiments that was done for examining the performance of the platinum loaded H-beta zeolite used for the hydroizomerization of hexadecenoic acid, will be explained. Then, in the second part of the research, experiments with iron loaded H-ZSM-5, aluminum fluoride, H-Beta, H-Mordenite, and H-Ferrieite will be described.

3.1 Experimental designs for Pt-H-Beta

The experimental performance using Pt-H-Beta were performed in four steps. First, replication of the literature data for hydroizomerization of palmitic acid by Pt-H-Beta was performed. Second, a design of experiments (DOE) was completed to identify significant factors. Third, a DOE was done in order to optimize the process by combining several factor levels of the most important parameters. Fourth, some single experiments were carried out on the basis of final points.

3.1.1 Replication

In order to check the reliability of our experimental procedure, replication experiments were carried out. To the best of our knowledge the only experimental work on hydroisomerization of palmitic acid had been done by Reaume *et al.*[12]. Therefore, the same protocol was used for catalyst preparation and experimental methods with 0.5wt%-Pt-H-Beta as the catalyst and palmitic acid as feedstock. As such, three replicates were done with the same procedure. Figure 44 shows the operating conditions of the three replicates.



Figure 44. Parameters for the three replicates

3.1.2 First design of experiments

The First DOE was developed to investigate the effect of other possible factors (such as platinum loading) on the zeolite support, the presence of water as a potential co-catalyst, the hydrogen pressure, and the temperature range (as listed in Table 11).

#	Temperature (° C)	Pt loading (wt%)	H ₂ Pressure (bar)	H ₂ O/Feed (wt%)
10	278	0.7	40	6.0
11	278	0.7	60	0
12	278	1.0	60	6.0
13	278	1	41	0
14	284	1	51	3.0
15	284	0.7	58	3.0
16	290	1	60	0
17	291	1	40	6.0
18	291	0.7	60	6.0
19	290	0.7	40	0

Table 11. Parameters for different experiments in the first DOE

In all of these experiments, the reaction time was 16 h, the catalyst to feed ratio was 3.5 wt%, and the stirring speed was set at 600 rpm. It should be mentioned that two center points were incorporated into this DOE (Experiment codes 14 & 15, listed in the Table 11).

3.1.3 Second design of experiments

A full factorial design of experiments was performed to optimize the process. Two key factors (temperature and catalyst/feed ratio) were already identified as the most important variables following the single experiments. As such, the second set of experiments was designed as a full factorial design in order to fully understand the behavior of the catalyst over various levels of every factor of temperature and catalystto-feed ratio. Table 12 details all combination of these factors for every experiment.

#	Temperature (° C)	Catalyst/Feed (wt%)
24	260	35
25	260	10
22	278	35
13	278	10
26	304	10
27	304	35
29	320	10
30	320	35

Table 12. Parameters for the second DOE

3.1.4 Single experiments

Some single experiments were also carried out to replicate the important experiments. Moreover, some other parameters were investigated such as feedstock effect in the form of an experiment using palmitic acid methyl ester. In addition, other one factor at a time experiments (OFAT experiments) were performed to investigate the effect of some operating parameters such as shorter reaction times and the stirring speed.

#	Temperature (° C)	Rxn. time (h)	Catalyst	Pt loading (wt%)	H ₂ Pressure (bar)	Catalyst/Feed (wt%)
1	288	4.5	Pt-H-Beta	0.5	7	30
2	278	16	Pt-H-Beta	0.5	40	22
3	288	4.6	Pt-H-Beta	0.5	7	29
4	285	16	Pt-H-Beta	0.5	40	25
5	295	6	-	-	40	0
6	278	6	Pt-H-Beta	0.7	40	22
7	278	16	Pt-H-Beta	0.6	40	22
8	278	16	Pt-H-Beta	0.6	40	22
20	290	16	Pt-H-Beta	0.5	40	35
21	278	16	Pt-H-Beta	0.5	50	10
22	278	16	Pt-H-Beta	0.5	40	35
23	260	16	Pt-H-Beta	0.5	40	45
28	279	16	Pt-H-Beta	0.6	40	45

Table 13. Operating conditions for the single experiments

3.2 Experimental plan for other catalysts

For another part of this research, some trials were done to examine the effect of a zeolite loaded with non-noble metal aiming at branching palmitic acids. H-ZSM-5 was impregnated with iron for this purpose and three other types of zeolite were examined ithout metal loading. At the end, one type of Friedel-craft catalysts (AIF₃) that had already been used in the hydroisomerization of short chain paraffins, was also tested.

A set of experiments was designed to explore the effect of the different catalysts. Table 14 details different parameters of various experiments.

Test #	Temperature (°C)	Rxn. time (h)	Cat. support	Promoting metal
1	200	4	AlF ₃	-
2	250	4	Hbeta	-
3	260	6	H-Ferrierite	-
4	280	6	H-Mordenite	-
5	240	2	HZSM-5	Fe
6	180	6	AlF ₃	-
7	280	6	HZSM-5	Fe
8	270	4	Hbeta	-
9	280	2	HZSM-5	Fe
10	290	6	H-Ferrierite	-
11	280	6	Hbeta	-
12	260	4	HZSM-5	Fe
13	250	2	Hbeta	-
14	290	4	HZSM-5	Fe
15	250	6	H-Ferrierite	-

Table 14. Operating condition of the experiments with Fe-H-ZSM-5, H-Mordenite, H-Ferrierite, H-Beta, and AIF₃

These experiments were all performed using the MRTB (explained in part 2.3.1). The heating rate for all experiments was 120 °C while the catalyst-to-feed ratio was defined as 5 wt% under a 6 bar hydrogen atmosphere for every experiment.

4 Results and discussion

In this chapter, the results from every set of experiments will be presented and discussed separately. As explained in Chapter 3, experiments were divided into two main sections. Therefore, first, results of the experiments with Pt-H-Beta and second, results of the experiments with other types of catalysts will be presented and discussed. However, the main focus will be on Pt-H-Beta since as mentioned in Chapter 1, the isomerization of the saturated hydrocarbon chain of palmitic acid needs a bifunctional catalyst to achieve branching reactions. Pt-H-Beta is a bifunctional catalyst and would perform better in lower temperatures if the promoting metal is a noble metal such as platinum.

Depending on the application three indications of conversion, selectivity, and yield were used to assess the performance of the catalyst. Since, in different fields there are some different definitions for conversion, selectivity and yield, to be more clear, these concepts, were defined as mass percentages from Pirola et al. [188]:

Mass conversion (wt%) =
$$\frac{98 - [palmitic acid in the product(wt% from GC - FID)]}{98}$$
3Selectivity= $\frac{Desired product(wt% from GC - FID)}{Mass conversion}$ 4Yield= $\frac{Desired product(wt% from GC - FID)}{Initial mass(wt% from GC - FID) \sim 98}$ or Yield=Mass conversion.Selectivity5

During the experiments, after separation of the product from catalyst and the solvent, the product was either a liquid or a solid at ambient temperature (see Figure 45). Yield of these products varied for each experiment.



Figure 45. Depending on the operating conditions final products were solid or liquid at the room temperature

The variation of yield could also be observed in Figure 46. For instance, as shown in Figure 46, second sample from left "Res.2020.023.017" had 78 wt% liquid yield; whereas, the last sample on the right "Res.2020.023.025" had 40 wt% liquid yield.

details the mass balance on the experiments. The "Volatile" column is related to the part of the material that was evaporated at ambient temperature during solvent removal under reduced pressure. As a result, the amount considered as volatile can also contain water that might have been removed via acetone in solvent removal procedure.



Figure 46. Variation of product yield in various experiments

	Gas(wt%)	Volatile(wt%)	Solid/liquid(wt%)	Tot(wt%)
1	2.0	9.0	89.0	100
2	10.9	42.8	46.4	100
3	4.8	28.8	66.4	100
4	1.2	9.7	89.1	100

5	4.2	24.9	70.9	100
6	0.6	3.4	96.0	100
7	1.2	10.2	88.6	100
8	1.6	19.7	78.7	100
9	2.8	13.1	84.1	100
10	2.0	2.7	95.3	100
11	2.9	13.3	83.8	100
12	1.4	4.3	94.2	100
13	6.9	15.2	78.0	100
14	4.3	12.1	83.7	100
15	2.0	8.7	89.3	100
16	4.6	20.0	75.4	100
17	3.4	5.1	91.4	100
18	2.9	1.1	96.0	100
19	3.7	10.9	85.4	100
20	5.4	32.6	62.0	100
21	0.9	2.2	96.9	100
22	7.4	15.7	76.8	100
23	2.6	12.4	85.0	100
24	4.6	13.0	82.4	100
25	3.1	5.1	91.7	100
26	5.1	29.6	65.2	100
27	15.1	31.0	53.9	100
28	17.0	34.9	48.2	100
29	5.4	14.1	80.5	100
30	22.8	37.6	39.6	100

As Table 15 demonstrates, there are significant differences in the final solid/liquid yields. These differences can cause considerable inaccuracies when it comes to comparison of the overall mass yield of every compound in different runs. Therefore, to calculate the final mass yield for every compound a two-step calculation was carried out. First, the mass percentage of every compound, was measured from area% in GC-FID. Next, this percentage was multiplied by the mass yield of liquid/solid to give the overall mass yield for each compound.

4.1 Pt-H-Beta

4.1.1 Replicate results

A triplicate was done to replicate the experiment of Reaume *et al.* in which they reported their optimum result [112]. The results of the triplicates and the mentioned reference have been compared in Table 16. It should be mentioned that the standard deviation between the results of the three replicates was less than 5% and the data in Table 16 is presented as an average.

Table 16. Comparing the results of the replicate

	Mass conversion	Mass selectivity	Isomer yield	CP reduction (°C)
Reaume et al.[112]	46	76	41	9.8
Replicate	5.7	72	3.6	8

Since the cloud point was not measured in this study, the 8 °C melting point reduction of the triplicates was considered as cloud point reduction. This is because melting point reduction has been deemed as a precise indicator of the cloud point[10].

The indicator of the catalyst performance in both studies has been the improvement of the cold flow properties. The 18 % difference between the results of the cloud point reduction could be attributed to differences in experimental set-up, measurement errors, etc. Therefore, the similarity between the final results validates the experimental procedure for the catalyst preparation and performing the experiments in this study. Another aspect to validate was the selectivity towards isopalmitic acids that was seen in agreement with a 5% difference.

However, there is a large diversity in mass measurement. This could be attributed to the fact that in this study, GC-FID was used to quantify the product. In fact, the area

percentage was the method by which the isomers were quantified. Whereas, in the reference study, isomers were quantified on the basis of a curve fitted based on palmitic acid peak in GC-MS. That leads to two controversies. First, GC-MS is not as effective as GC-FID for quantification means. Second, branched fatty acids have different spectra [33] and using the curve of mother molecule (hexadecenoic acid) to quantify them, could end up with large errors. In addition, reported data in a U.S. patent that was registered by Keneally et al. [21] for a similar process including isomerization of stearic acid by 0.5 wt% Pt-H-Beta supports the actual work since the maximum yield is reported in the mentioned patent as 5.4%.

In summary, the results of the replicate were confirmed by the reference study. However, when it comes to catalytic experiments, many parameters could be considered for probable effects on the yield of desired as well as undesired products. Catalytic experiments on the hydroisomerization of palmitic acid is not an exception. To investigate the process in depth, possible parameters were defined as listed in Figure 47.





These factors were investigated through 3 different phases of a fractional factorial designed set of experiments, a full factorial one and single experiments.

4.1.2 Results and discussion on first set of designed experiments

First DOE was performed in order to investigate the effect of four fundamental factors. Temperature, initial hydrogen pressure, water presence as a potential cocatalyst, and platinum loading. After a factorial regression suitable statistical analysis confirmed the validity of the model (Table 17).

S	R-sq	R-sq(adj)	R-sq(pred)
0.423379	97.57%	95.63%	93.73%

From the results of the model, it was concluded that water had an extremely negative effect instead of having positive effects (such as being a co-catalyst). This is shown in Pareto chart of Figure 48.



Figure 48. Pareto chart showing the significant effectiveness of water presence

Another conclusion from the pareto chart was low effects of Pt loading, hydrogen pressure, and temperature. As a result, apart from temperature they were excluded from parameters to be investigated in the following experiments. The 40 bar pressure that was in agreement with the results obtained by Reaume et al.[12], was selected as the reference pressure, and the catalyst with the higher platinum to support ratio (1) was selected as the catalyst of choice for the next set of experiments.

However, in catalytic studies the effect of temperature has always been among the most significant parameters. Therefore, it was interpreted that there must have been an error in selecting the high level and low level in the screening experiments that was investigated in the following experiments.



Figure 49. Main effect plot for isopalmitics as response

Among these experimental runs, trial number 13 resulted the highest amount of yield towards isopalmitics (Figure 50). 5.7 yield was obtained at 278 °C, 40 bar, 0 wt% water/Feed, and with 1wt% platinum/support loading.



Figure 50. Yields of isopalmitics in the first set of experiments

4.1.3 Results and discussion on second set of designed experiments

The second set of experiments were designed and performed to fully investigate the role of temperature and catalyst/Feed ratio. The selection of temperature was done in order to discover the performance of the catalyst by increasing and decreasing the conversion in comparison with the first set of experiments. This way, the effect of conversion of palmitic acid on the selectivity and yield of isopalmitics was studied as well (See 3.1.3 for information about the DOE). After a factorial regression suitable statistical analysis confirmed the validity of the model (Table 18).

Table 18. Model summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.746659	97.20%	94.75%	88.81%

The first output from the model illustrates the significance of the two factors of temperature and catalyst/feed with a P-value of almost zero. This validates the selection of the mentioned factor for an in-depth study to improve the yield of hydrosiomerization reaction.



Figure 51. Pareto chart of the standardized effect

Figure 52 presents the result of the model that was developed based on the data from the experiments. The contour plot demonstrates that the highest yield of the hydroisomerization is when the catalyst-to-feed ratio is more than almost 23 wt% and temperatures between 260 to 278 °C. Unlike the previous studies [12], output of this analysis uncovered that the hydroisomerization was a compromise between catalyst-to-feed ratio and temperature. In other words, by increasing the catalyst-to-feed ratio the

same yield could be obtained at lower temperature. Therefore, the application of this could be in plant design and economic studies whether to achieve the target yield by higher temperature and lower catalyst-to-feed ratio or vice versa.



Figure 52. Contour plot of isoplamitics's yield versus temperature and catalyst/Feed

The result of the model is illustrated also in Figure 53 as a surface plot. The surface plot demonstrates a dramatic fall in yield of the hydroisomerization after 278 °C when the catalyst/feed ratio is at 35 wt%. In fact, at this ratio, from 300 °C onwards the yield of the hydroisomerization is equal to zero. But at just 20 °C less the yield reached its maximum. Then at 20 °C less than 278 °C the yield decreases just by 15%. This is in line with the studies on the hydrocarbon hydroizomerization processes suggesting that the hydroizomerization of long linear chain hydrocarbons has higher yields at temperatures lower than the ones at which it starts to be cracked. In other words, to supply the activation energy and low enough to not promote the cracking reactions which has a better kinetics at higher temperature.



Figure 53. Surface plot of iPA yield versus operating temperature and catalyst/feed ratio

The fact that higher temperatures can speed up the production of isopalmitcs as well as 1st side products, can be observed by a comparison between Figure 55 and Figure 56. Figure 55 clearly demonstrates the highest yield of isopalmitcs at 278 °C, whereas Figure 56 demonstrates the highest selectivity of isopalmitcs at 260 °C. Higher selectivity stems from lower amount of side reactions such as decarboxylation and hydrodeoxygenation and formation of aromatics that will be discussed in detail in the following paragraphs. Response optimization of the model showed that at 260 °C and 35 wt% of C/F ratio there is maximum hydroisomerization while the decarboxylation, hydrodeoxygenation and reforming are at their minimum level.



Figure 54. Response optimization as one of the outcomes of the model



Figure 55. Yield of iPA at C/F 35%



Figure 56. Selectivity of iPA at C/F 35%

Figure 57 lists all the products that were detected by GC-MS and micro-GC. In continue every side product shown in Figure 57 will be discussed separately.



Figure 57. Detected products in all experiments

Pentadecanes are long linear chain hydrocarbons that could be used as drop-in green diesel. Pentadecanes, in this case, should be the product of a reaction known as decarboxylation. Decarboxylation is the side reaction in which palmitic acid is cleaved and carboxylic group is lost in the form of CO₂ which can be associated to the presence of platinum on the catalyst support. The production of a long chain alkane from a fatty acid in parallel with hydroisomerization reaction without hydrogen consumption, unlike a hydrotreating process, could be an advantage in biorefineries. Figure 58 indicates that the yield of decarboxylation reaches its maximum amount at 278 °C and falls dramatically at higher temperatures. The decrease of yield, with the increasing temperatures is related to the cracking of the long hydrocarbon chains that are more prone to cracking with a temperature rise rather than shorter chain hydrocarbons.



Figure 58. Yield of C15 & C16

Another side product that was detected is hexadecane. The importance of hexadecane production stems from definition of cetane number for diesel fuel based this compound. Therefore, it could be used and sold as an important value-added by-product. However, as this side reaction (equation 6), consumes hydrogen and depending on the economics of the plant it might be favorable to select the operating conditions to minimize it.

$$R \xrightarrow{\bullet} R \xrightarrow{\bullet} R \xrightarrow{\bullet} CH_3 \xrightarrow{\bullet} 2H_2O$$

Aromatics were the other by-products and the latter occurred in three major categories, namely alkyl Benzenes, alkyl naphthalenes, and alkyl phenanthrenes. It should be mentioned that during solvent removal there were always a loss of material that, after analysis of the removed solvent, turned out to be aromatics. The removed material's weight was considered along with the mass fraction of aromatics quantified by GC-FID for aromatics' yield calculations. Figure 59 shows the yield of aromatics based on the GC-MS and GC-FID results, combined with the weight loss during the product extraction. From Figure 59 can be seen that aromatics reach their maximum at 300 °C. However, there is a decrease in the yield after 300 °C which is probably due to the rise of non-condensable gases that could be observable in Figure 60. Production of non-condensable gases increases exponentially with increasing the temperature.



Figure 59. Yield of aromatics (wt%) versus temperature (°C) at 35 wt% of C/F



Figure 60. Yield of non-condensable gases

4.1.4 Single experiments

Single experiments were carried out to investigate the changes in some of the parameters such as the reaction time, the removal of the catalyst, changing the zeolite support and stirring speed as well as examining the activity of the catalyst over methyl ester form of palmitic acid (PAME).

To ensure that the hydroisomerization is exclusively an acid-catalyzed reaction, an experiment was carried out where the operating temperature was set at 278 °C. In addition, reaction last for 16 h, and reactor was kept under 40 bars of H₂ atmosphere, and stirring speed of 600 rpm. The results from GC-MS and GC-FID, confirmed that the final product contained only 0.1 wt% of the isopalmitics that were already present in the feedstock. This experiment confirmed the fact that similarly to alkanes the hydroisomerization of long chain fatty acids (such as palmitic acid) is an acid-catalyzed reaction and production of isopalmitics through a thermal process is impossible.

The next experiment was intended to see the impact of the catalyst support to H-Ferrierite as it was proven to be a high-performance catalyst for the isomerization of unsaturated fatty acids such as oleic acid or even its ester forms (oleic acid methyl ester). Hence, H-Ferrierite was loaded with 0.5 wt% platinum was examined at the temperature of 278 °C, for 16 h, under 40 bars of H₂, and with a stirring speed of 600. The results both from theGC-MS and GC-FID, showed just 0.3wt% isopalmitics demonstrating a very low activity at C/F of 5 wt%.

The reaction time was the next parameter to be investigated via single experiments. 0.7 wt% Pt-H-Beta zeolite was employed at a C/F ratio of 22 wt%. The operating conditions were 278 °C, 40 bar H₂, with a 600 rpm stirring speed for both experiments. For experiment 6 and 8 (see section 3.1.4) the reaction time was 6 and 16 h, respectively. The results from the GC-MS and GC-FID, uncovered a 50 wt% isopalmitics yield increase from 3.3 wt% to 5 wt% (see Figure 61).



Figure 61. Effect of reaction time on the yield of isopalmitics

Another experiment aimed of examining the activity of Palmitic acid methyl ester, which was used to determine the activity of 0.6 wt% Pt-H-Beta zeolite in ester form (palmitic acid methyl ester). The reaction was performed at 278 °C, for 16 h, under 40 bar of H₂, and stirring speed of 600 rpm. Results showed a high activity of the catalyst over the ester form as the conversion was 100 wt% (see Figure 62). However, due to an extreme activity the whole starting material was converted to aromatics and non-condensable gasses.



Figure 62. Higher catalyst activity over the ester form

The result of this experiment suggests that a set of experiments could be designed and carried out to investigate in-depth the operating conditions at which the yield of hydroisomerization for the palmitic acid methyl ester using 0.5 wt% Pt-H-beta is higher. The result could be fruitful for industrial applications where the trans-esterified saturated fatty acids could directly serve as feed for hydroisomerization. In other words, trans-esterification of triglycerides followed by hydroisomerization of saturated fatty acids would be a more convenient pathway as compared to hydrolysis, hydroisomerization of saturated fatty acids, and finally esterification of isomerized fatty acids.

The effect of the catalyst/feed ratio on the yield of isopalmitics was investigated by experiments at three different catalyst/feed ratio of 10 wt%, 35 wt%, and 45 wt%. The operating temperature was kept at 260 °C, for 16 h, under 40 bars of H₂, and a 600rpm stirring speed. The catalyst was 1 wt% Pt-H-Beta for the experiments. Figure 63 shows that the yield of isopalmitics increases from 4.6 wt% to 7.7 wt% which is a 67 % improvement, although it also shows that increasing the catalyst to feed ratio does not necessarily improve the yield, as the yield falls dramatically at the catalyst/feed ratio of 45 wt% to 3.8 wt%.


Figure 63. Effect of catalyst /Feed ratio on the yield of isopalmitic acids

An experiment at 6.8 bar versus 40 bar as well as shorter reaction time of 4.5 h instead of 6 or 16 h was performed to see the result of shorter reaction times and lower hydrogen initial pressure. This extremely could influence the economics on any downstream industrial application. The result showed a 4 wt% yield towards isopalmitics. The influence of this level of isomerization yield on reducing the melting point of the product will be discussed later. Figure 64 illustrates a comparison of the isopalmitics' yield between the experiment with the highest yield and this experiment. In comparison with the former, this experiment has been kept at the reaction conditions 11.5 h less as well as an almost 33 bars lower hydrogen pressure. These differences in the operating conditions and a 5.1 wt% difference between the yields should be investigated in the future works to see if the profits justify the operating and capital costs. Longer reaction time demands a higher energy supply. Moreover, operating pressures higher than 20 bar induces higher operating/capital costs and demands higher safety measures.



Figure 64. Comparison between the best result (under 40 bar hydrogen, reaction time 16 h) the experiment with shorter reaction time and lower initial pressure of hydrogen (under 6.8 bar hydrogen, reaction time 4.5 h). Both experiments were performed on palmitic acid and using the 1 wt%Pt-H-beta.

4.2 Other catalysts

The experiments on the other catalysts namely HZSM-5, Fe-H-ZSM-5, AlF₃, H-Mordenite, H-Ferrierite, and H-beta were performed mainly on zeolite supports to observe their performance for the isomerization of palmitic acid. In addition, AlF₃, considered as a traditional catalyst for the isomerization of short chain alkanes (known as Friedel-Craft catalyst) was examined, too. Moreover, the effect of non-noble metals on solid acid zeolites, iron impregnated HZSM-5 was also investigated. For these experiments, only the melting point and acid value were chosen as means of measuring the catalyst performance. Table 19 lists the best results attained for the other catalyst in addition to the blank test performed without any catalyst.

	Catalyst	T (°C)	P(bar)	t(h)	MP (°C)	A.V. mg KOH/g prod
T ₀	-	280	2	6	63.0	220
T ₄	H-Mordenite	280	6 H ₂	6	62.8	215
T ₁₀	H-Ferrierite	290	6 H ₂	6	62.5	210
T ₁₁	H-beta	278	24 Ar	6	62.0	205
T ₆	AIF3	181	28 Ar	6	61.2	200
T ₇	Fe-H-ZSM-5	280	6 H ₂	6	60.0	190

Table 19. Operating conditions

The best result showed a 3 °C improvement when using the bifunctional catalyst Fe-H-ZSM-5. However, an acid value of 190 mg KOH/g sample could mean that part of this improvement could have been due to the decarboxylation of palmitic acid (14 wt% decarboxylation) and not the isomerization of palmitic acid. Furthermore, in these experiments, there was no agitation which is crucial in catalytic experiments to promote the chemical kinetics. Hence, it was concluded to modify the MRTB set up with a pressured stirred Parr engineering autoclave as well as impregnating the support with a noble metal.

4.3 Melting point reduction

One of the most important aims of this research was to define the effect of isopalmitics' share in the reduction of melting point of the post-reaction mixture. Since hydrocarbons were present in all samples, three products were chosen as follows (Table 20):

- 1. The sample with almost 0 wt% of isopalmitics, 4.4 wt% of C15-C16, and 95.6 wt% of palmitic acid
- 2. The sample with 5 wt% of isopalmitics, just 1 wt% of C15-C16, and 94 wt% of palmitic acid
- 3. The sample with 9 wt% of isopalmitics, 3.1 wt% of C15-C16, and 87.6 wt% of palmitic acid

Sample number	PA	iPA (wt%)	HCs(wt%)	MP	MP
					reduction
					(°C)
1	95.5	0.1	4.4	61.0	2.0
2	94.0	5.0	1.0	53.0	10.0
3	87.6	9.3	3.1	43.0	20.0

Table 20. Composition of three different samples and their melting point measurement results

After measuring the melting point of the three samples (reported in Table 20), a multiple linear regression yielded the equation (7):

According to this equation, every weight percentage of the isopalmitics can cause almost 2 °C degrees of melting point reduction when mixed with non-branched palmitic acid, whereas every percentage of C-15+C-16 can decrease the melting point of the mixture up to 0.5 °C. Thus, it could be estimated that every percentage of isopalmitics is approximately four times more effective in reducing the melting point of the mixture after the addition to the mother compound (palmitic acid). In fact, in sample 3, 9.3 wt% of isopalmitics should have caused an 18 °C reduction and 3.1 wt% of hydrocarbons just led to a 2 °C (out of 20 °C) of melting point reduction.



Figure 65. Effect of isomerization in lowering the melting point of the product

4.4 Expanding on the results

In this part, the result of experiment 22 (see section 2.3.2 & 3.1.3) will be discussed. This experiment is targeted here since it has the highest overall isomerization yield among the whole tests that were performed (Figure 66).



Figure 66. Overall yield of isopalmitics considering lost starting material in the form of non-condensable gases and evaporated volatile material

Figure 64 shows the parameters and operating conditions for this reaction while Figure 68 illustrates the phase balance for experiment 22. As mentioned before, the volatiles were lost during the solvent removal. However, the collected solvent was analyzed by GC-MS after a reduced pressure extraction and turned out to have extracted the aromatics from the product. In addition, it could have extracted the water produced from hydrodeoxygenation that could be subject of future work to be determined precisely.



Figure 67. Parameters and operating conditions of the experiment 25

Figure 68. Phase balance of the experiment 22



Figure 69. Distribution of the process outlet in wt%

As it could be seen in Figure 70 the final product was in liquid phase at ambient temperature which could be related to almost 12 wt% of isopalmitcs and 14 wt% of long chain linear alkanes despite containing almost 75 wt% palmitic acid.



Figure 70. Final product that despite containing 75 wt% palmitic acid was in liquid phase at ambient temperature

4.4.1 Discussion on the liquid phase

The GC-MS and GC-FID analysis are presented in Table 21. As discussed in section 4.1.3, 3.4 wt% hexadecane should result from the hydrodeoxygenation as one of the

side reactions. Also, a 10 wt% of n-C₁₅ should be found as a result of the decarboxylation side-reactions. A total of 12 wt% of the liquid phase was defined to be isopalmitics. The impact of about 12 wt% isopalmitics and 13 wt% long chain alkanes is so significant that it made the blend containing 75 wt% of palmitic acid to a liquid at room temperature. This could be highly interesting for industrial applications when it comes to undergoing a subsequent esterification step. In other words, the final blend from hydroisomerization process containing 87 wt% of palmitic acid and its isomers could drop another almost 30 °C after esterification. The rest (13 wt% hydrocarbon) is also perfectly in line with biofuel standards to be used in biodiesel blends.







Figure 71. Distribution of the compounds in the liquid phase

4.4.2 Gas phase

The gas phase analysis was carried out in order to quantify the hydrogen consumption while providing an estimation of the compounds that could possibly provide energy back to the plant if such process was to be scaled up. Results confirmed the theory on literature on very low hydrogen consumption due to almost 3 % of hydrodeoxygenaton reaction.



Figure 72. Composition of gas phase in wt%

The 42 wt% of hydrogen found in the final gas-phase (see Figure 72) shows that in light of the 0.4 g hydrogen that was injected to the autoclave, almost 1 g hydrogen was collected at the end of the process. This result means that hydrogen is being produced in the process which could be justified by the aromatization and cyclization reactions [189] shown in equations 8 and 9.



4.4.3 Volatile compounds

The GC reported several peaks corresponding to different compounds that were not identified by the mass spectra library. Some of them could have been identified as cyclic and aromatic hydrocarbons (benzenes and naphthalenes). These peaks were observed either from the separated solvent after product extraction, or from the extracted product. If this process was to be scaled-up based on this result, the volatile part, could be evaluated as potential added-value compounds such as bio-aromatics, that would have wide applications in the chemical industries.

4.4.4 Identification of isopalmitics

The identification of the isomers was of interest to identify the type and if they were mono or multi-branched. This is a key issue effect of the isomers in reducing the melting point as multi-branched compounds are more effective for this issue. As such, Junaid et al. [190] analyzed the multi-branched isomers to be as high as 96% (Figure 73). Such high percentage of multi-branched isomers might have been due to the long reaction time of 16 h used in their work. This agrees with the results of Regali et al. [191] revealing that for the isomerization of n-C₁₅, with increasing the conversion, the selectivity towards multi-branched isomers was increasing compared to mono-branched isomers.



Figure 73. Identified isomers [190]

This result, was considered in the case study for further modeling and technoeconomic analysis since, the bio-based approach of this process could offer a process towards biofuels. The other byproducts in this case would be off-gasses that the C_1 - C_4 that could provide energy back to the system, as well as bioaromatics as value-added materials.

4.4.5 Result and discussion on the characterization of the catalyst

4.4.5.1 Scanning Electron Microscopy (SEM)

Once the preparation was done, the catalyst was analyzed using scanning electron microscopy to ensure the presence, dispersion, and concentration of platinum particles on the support surface. The white points in Figure 74 depict platinum particles that have been placed on the surface of the zeolite.



Figure 74. Scanning electron microscopy on Pt-H-Beta

As shown in Figure 75, the SEM instrument has detected the presence of platinum atoms.



Figure 75. Detected catalyst elements by SEM

Another aspect of importance in characterizations was to define dispersion of the platinum on the support surface. Figure 76 indicates that the platinum was well dispersed on the zeolite surface. Platinum dispersion is illustrated in Figure 76 as red spots.



Figure 76. Dispersion of atoms

One of the parameters to be investigated was also weight concentration of the platinum that according to the report from SEM analysis almost 1 wt% weight concentration of Pt was confirmed as desired concentration during impregnation step (detailed in Table 22)

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	0	Oxygen	72.57	59.53
14	Si	Silicon	24.83	35.76
13	Al	Aluminum	2.42	3.35
78	Pt	Platinum	0.12	1.17

Table 22. Atomic concentration and weight concentration of elements

Platinum agglomerates were also measured for several catalyst particles by scanning electron microscope (Figure 77). Several measurements resulted in a range between 33 nm up to 264 nm which is in line with the results from Reaume et al[10].



Figure 77. Measurement of Pt agglomerates

In general, SEM analysis confirmed the desired dispersion and concentration of the platinum on the support of the catalyst.

4.4.5.2 Physical adsorption (N₂ adsorption)

The aim of the physical adsorption analysis was to determine the surface area of the catalyst and compare it with the claimed surface area by the manufacturer. An isotherm was obtained after the analysis that has been presented in Figure 78. The surface area for beta zeolite coded as CP 814E with a SiO₂/Al₂O₃ molar ratio of 25, had been reported as 680 m²/g. The analysis suggested a surface area of 520 m²/g. 24% difference between the results can stem from the fact that the instrument that was used for this analysis was mostly decent for meso- and macro-porosity rather than micro-porosity.



Figure 78. Isotherm curve from physical adsorption

In conclusion, surface area from physical adsorption analysis agreed with the surface area claimed by the zeolite manufacturer.

4.4.5.3 X-Ray Diffraction (XRD)

The diffractogram of beta zeolite (Figure 79) was compared and matched with the Beta framework in Pearson's Crystal database. The diffractogram was also compared with the PXRD result of the same catalyst characterized by Mendes et al. [192] (Figure 80).



Figure 79. XRD powder diffractogram of HBeta used in the experiments



Figure 80. XRD powder diffractogram of HBeta zeolite from Mendes et al.[192]

4.4.5.4 Thermal gravimetric analysis (TGA)

The goal of thermal gravimetric analysis was to define if the ammonium had been removed after calcination step during the Pt-HBeta synthesis. For this analysis two samples were prepared. First sample was uncalcined beta zeolite containing ammonium and the second sample was calcined beta. Figure 81 demonstrates that when the temperature reaches at 320 °C (the temperature at which ammonium starts migration to the gas phase), the uncalcined beta begins to considerably lose weight (2 wt%). While, calcined catalyst that is indicated in Figure 81 with black color does not show a significant loss of weight (less than 0.2 wt%). This result suggests that the method for the calcination (see section 2.2.2) has correctly been exploited for removal of the ammonium and conversion of Lewis beta to Brønsted beta.



Figure 81. TGA graph for calcined (black) and non-calcined (red) beta zeolite

In conclusion, characterization of the catalyst confirmed the required specifications of a bifunctional catalyst that was desired for performing the hydroizomerization reaction. Results indicated that the support had the structure as beta zeolite. Surface area of the catalyst support was determined as well. It was also concluded that the ammonium had been successfully removed from the Lewis from of the zeolite beta by calcination. Then the platinum presence and its well dispersion on the surface of the support was confirmed.

5 Modeling, energy and economic assessment

In order to set the stage for the realization of a commercial plant, process modeling could provide a variety of fundamental information on the process economy and feasibility in light of its technological aspects. Furthermore, it provides the advantage of recognizing and optimizing the process for its most important and sensitive while also contributing to the overall process optimization [193]. For the simulation part of this work, continuous mode was selected over a batch one. There are some advantages in established continuous plants such as the improved liability for automatically controlling the operations and instruments, a superior quality of control capabilities, decreased expenses of labor, and a generally more stabilized operating conditions [14].

5.1 Modelling

In this part, the simulation of a biodiesel plant modified with an isomerization unit will be explained. To simulate, the most recent version of a common engineering program known as "Aspen plus" produced for designing chemical processes was used. Aspen plus was used because of its up-to-date as well as comprehensive database of chemical compounds. For instance, the isopalmitic acid methyl ester was extracted from Aspen Plus' database in this simulation.

The simulation is composed of 9 main units as follows (Figure 82):

1. Transesterification of palm oil

Input of this model is based on a realistic vegetable oil feed such as palm oil rather than an ideal model compound such as triolein. The composition of the palm oil has been obtained from Che Man et al. [194] representing a palm oil that has previously been refined, bleached, and deodorized. Palm oil is defined as a combination of triglycerides containing oleic acid, palmitic acid and myristic acid that, after transesterification, are released as their corresponding fatty acid methyl ester. This stream is illustrated in Figure 82 as "Oil" with a flowrate of 1050 kg.h⁻¹. Then, there is the stream called "NAOH" representing the alkali homogenous catalyst used for transesterification reaction. The flowrate of sodium hydroxide is set as 50 kg.h⁻¹. The next stream is called "MEOH" which is methanol used as reactant for the transesterification of vegetable oil. This stream is manipulated by a design specification that adjusts the flow rate of methanol in the "MEOH" stream so that in the mass fraction of the methanol in the outlet stream of the transesterification reactor would have just a quantity of 0.092 m/m. This way, the methanol flow rate is adjusted automatically as the reaction demand thus avoiding high expenses with the plant scale up. The temperature and pressure for the reaction were fixed at 60 °C and 4 bar respectively. In addition, a 1 h residence time was set for this unit.

2. Recovery of unconverted methanol

According to the different boiling temperature between methanol and the other compounds in the mixture, the excess methanol can be separated via a distillation column with seven trays and after condensation could be recycled back to the transesterification reactor.

3. Washing

Downstream of the distillation unit named "EST1" is a combination of fatty acid methyl esters, unconverted palm oil, sodium hydroxide, and glycerol. In light of the solubility of glycerol and sodium hydroxide in water and at the same time, the immiscibility of fatty acids, a liquid-liquid extractor separates the fatty acids and their methyl esters. The latter leave the unit as the upstream named "EST4" while the rest of the material exit the unit by the stream "AQU1". The flowrate of water to this unit is 50 kg.h⁻¹.

4. Distillation

In this unit, a distillation column allows the separation of the esters from the unconverted triglycerides. FAMEs are transferred to the next step as the stream "FAME", and unconverted tryglycerides are recycled back to the feed via stream names as "OILREC".

5. Neutralization of the catalyst

In the aqueous phase, to remove the catalyst (a base), phosphoric acid is fed to a RSTOIC reactor to react with sodium hydroxide and precipitate the resulting salts. Subsequently, a filter separates the solids form liquid.

6. Purification

The purification unit named as "GLYCEROL", separates water from glycerol through a distillation column with 6 stages. The produced glycerol has a flowrate of 114 kg.h⁻¹.

7. FAME separation

In order to separate the saturated methyl esters which are the palmitic acid methyl esters from the unsaturated fatty acids methyl ester, a distillation tower with 32 trays is used and the latter is named "FAMESEP" on the simulation. The downstream of this operation unit is oleic acid methyl esters with a flowrate of 490 kg.h⁻¹ while the upstream contains saturated fatty acid methyl esters mainly palmitic acid methyl esters.

8. Hydroisomerization of SFAME

The upstream from step 7(FAME separation) is sent to the hydroisomeizator, fed with hydrogen and another stream of catalyst. The catalyst stream is filtered and recycled back to the reactor after the reaction. Hydrogen that is fed to this unit and is just consumed in very minute quantities. In fact, the hydroisomerizator reactor is designed based on the results from experiment 22 that was explained in detail before (see section 4.4).

9. Separation

The last separation unit is composed of a flash drum used to separate the gases and a subsequent distillation column allowing separation volatile materials (here assumed benzene), hydrocarbons, and isomethyl palmitates.



Figure 82. The scheme of the biodiesel plant modified by an isomerization unit

5.1.1 Model results

Results of the model are presented in this part as material and energy balance as well as an economic analysis.

5.1.1.1 Mass balance

This section presents the mass balance of the input and output streams of the model. Table 23 lists the flow rates of all the streams in Figure 82.

Stream name	In (kg.h⁻¹)	Out (kg.h ⁻¹)
NAOH	50	
Phosphoric acid	41	
MEOH	127	
OIL	1050	
Water	50	
Hydrogen	2.6	
WaterMEOH		133
MEOHWAT		5
Solid wastes		14
Glycerol		114
PAME		326
iPAME		52
C ₁₆		15
C ₁₅		43

Table 2	3. Mass	balance	for inlet	and outlet	streams

H ₂ O		2
Benzene		88
CH ₄		1
CO ₂		19
C_2H_6		1
C_3H_8		10
C_4H_{10}		8
OAME		490
Sum.	1321	1321

5.1.1.2 Energy balance

The energy balance resulting from the model on the basis of every piece of equipment's energy demand are presented in Table 24. It should be mentioned that negative sign in some rows is due to losing energy such as energy loss in condensers.

Unit operation name	Q (kW)	W (kW)
Heat exchanger 1	22.1	
Reactor 1 (Esterification unit)	15.0	
Distillation 1 (Condenser)	-121.9	
Distillation 1 (Reboiler)	117920	
Pump 3		.1
Distillation 2 (Condenser)	-304.3	
Distillation 2(Reboiler)	373.1	
Distillation 3 (Condenser)	125.9	
Distillation 3(Reboiler)	254.0	
Reactor 2 (Hydroisomerizator)	4.5	
Distillation 4 (Condenser)	-65.6	
Distillation 4(Reboiler)	84.8	
Distillation 5 (Condenser)	-261.1	
Distillation 5(Reboiler)	283.8	
Reactor 3	-1.5	
Heat exchanger 2	-9.5	
Total	51	.7.5

Table 24. Energy balance for various unit operations

5.1.1.3 Economic analysis

5.1.1.3.1 Capital cost

Equipment cost for every piece of equipment was calculated by summation of depreciated commercial price (10 years depreciation), related taxes (excluded), insurance charges (0.8 % of the equipment cost), as well as maintenance expenses (3 % of the equipment cost), overall costs of the plant (0.75 % of the equipment cost). The expenses for potential future required pieces of equipment (15% of the equipment cost). Then, the calculated number from summation of all facilities was added to another 15% of the obtained figure multiplied by 3 to yield the total capital costs including the construction costs such as installation and engineering costs [193]. The cost estimates were extracted from the Aspen plus database.

Capital cost for every equipment= depreciated commercial price+ related taxes (excluded)+ insurance charges (0.8 % of the equipment cost) + maintenance expenses (3% of the equipment cost) + overall expenses of the plant (0.75 % of the equipment cost)

Total capital cost=3*((summation of capital costs for every piece of equipment)+ 0.15*(summation of capital costs for every piece of equipment)) [193].

5.1.1.3.2 Operating cost

The materials, utilities, labor, and equipment-related expenses represent the operating costs [193]. In a simulation for the isomerization of oleic acid done by Helen et al. [193], the cost of oleic acid was defined as U.S. \$ 1.66 kg⁻¹ by summation of U.S. \$ 0.99 kg⁻¹(bleached fancy tallow) + U.S. \$ 0.66 kg⁻¹ (conversion and losses) accounting for 64% of the operating cost [195]. By their calculations, the catalyst, which was a Ferrierite zeolite with a 5 times reusing cycle, accounted for almost 11 % of the total operating cost. Now, if we assume the necessity of 0.5 wt% and 0.1 wt% platinum doped Ferrierite zeolite instead of a simple one in the process, the amount required for a year would be 28144 kg, therefore 140.72 and 28.14 kg Platinum is needed respectively. With an approximate price of U.S. \$ 160 g⁻¹ platinum, and assumption of 0.5 wt% and 0.1 wt% pt doped Ferrierite as well as an assumption of utilization of catalyst for just 5 cycles,

share of catalyst in operating costs rises to 65 % and 32 % respectively from a 11 % which is related to using Ferrierite only. According to our calculations (demonstrated in Figure 83), these numbers drop to 26 % and 8 % respectively when the cycling frequency is considered to be 26 cycles.year⁻¹. It should be mentioned that Ferrierite has already shown a significant activity even after 20 times of reutilization [14]. For Ferrierite after 8 cycles, the product cost had less than a 1 % decrease. Whereas, this decrease is obtained after 26 cycling times for 0.5 wt%PtFerrierite and 14 for 0.5 wt%PtFerrierite. In addition, operating costs increases to almost 37 and 19 M\$ respectively from 14 M\$ for a simple Ferrierite zeolite, considering a 5-cycle catalyst reusing. These numbers change to 17, 14, and 13 M\$ in case of reusing 26 times the catalyst per year respectively. These show the effect of utilization of catalysts containing noble metals in an industrial plant as well as effect of renderability characteristics on economics of the process.



Figure 83. Influence of catalyst reutilization on the production cost

5.1.1.3.3 Other parameters to be considered

Some parameters are to be considered for the capital and operating costs which are the exterior environment of the unit operation. The capital dedicated to laboratories, office buildings, related utilities, water treatment facilities, controlling tools of air pollution, or transport facilities such as railroad tracks infrastructures, working capital, money cost, taxes on incomes and credits and return of investment are important aspects to be considered as well.

In the end Table 25 lists the result of the economic assessment. Payout period was calculated as 10 years.

Total Capital Cost [USD]	10513900
Total Operating Cost [USD/Year]	8417520
Total Raw Materials Cost [USD/Year]	5715580
Total Product Sales [USD/Year]	12101400
Total Utilities Cost [USD/Year]	159929
Desired Rate of Return [Percent/'Year]	20
P.O. Period [Year]	10.0024
Equipment Cost [USD]	1127500
Total Installed Cost [USD]	4379600

Table 25. Result of the economic analysis

6 Conclusion

The present work reviewed, studied and demonstrated the production of isomers through the hydro/isomerization process using environmentally friendly catalysts. The result from a comprehensive literature review allowed the consideration of a large number of catalysts for the hydro/isomerization processes. In addition, the review demonstrated the similarity between the three groups of feedstock and also similarities between the used catalysts for the hydro/isomerization of every feedstock.

The most promising hydro/isomerization bi-functional catalysts for the three categories of feedstock namely saturated/unsaturated long linear chain fatty acids as well as long linear chain alkanes was identified as Pt-H-Beta. Therefore, the major part of this study turned around Pt-H-Beta and consequently, the best results were obtained by using this catalyst. However, as the second category a Friedel-craft catalyst, four zeolites, and one zeolite loaded with a non-noble metal were examined as well.

Experiments on the second category of catalysts was performed using a micro reactor test bench and did not show satisfying results. The best result was the melting point reduction of the product by up to 3 °C which was considered as a promising step forward for using non-noble metals for the first time in isomerization of long chain linear fatty acids. However, the results still did not fulfill the target of the study. Another conclusion was that there was not sufficient mixing in the MRTB set-up.

The first replicate experiments performed using an autoclave with 0.5 wt% platinum loaded H-Beta zeolite led to an 8 °C reduction of the melting point as compared to 9.8 °C observed in the reference study. This result validated the catalyst preparation methods and the experimental procedure due to 18 % difference that was justified in the relevant section. It was also concluded that derivatization technique before injecting the sample into the GC-MS and GC-FID was a must for the detection and quantification of isomers. Other experiments, carried out with higher platinum loadings on H-Beta showed best results. Investigating higher loadings of H-beta was performed for the first

time (to the best of our knowledge). The highest obtained yield of isopalmitics was 9.1 wt% when the operating temperature was fixed at 278 °C, after 16 h, under 40 bar of H₂, and 100 rpm stirring speed. This study also developed and presented an empirical correlation for the prediction of mixture melting point reduction when the sample contains palmitic fatty acid, branched palmitic acids, n-hexadecane, and n-pentadecane. This work revealed that in order to reduce the melting point of palmitic acid, blending with branched isopalmitcs would be 4 times more effective as compared to blending with the same percentage of long chain hydrocarbons (n-C₁₅ & n-C₁₆).

Other very important parameters were also identified to be the hydrogen pressure, water presence, and catalyst to feed ratio. It was shown that very high or very low pressures of hydrogen did not necessarily favor the hydroizomerization of palmitic acid. Instead, there was an optimum operating pressure for obtaining the best result. Experiments showed that the presence of water had a deteriorating effect when using Pt-H-Beta catalyst for the hydroizomerization reaction. Moreover, the importance of catalyst to feed ratio was studies that had not been investigated in the similar previous studies. Thanks to modeling of the results, our findings suggested that there was a relevance between catalyst/feed ratio and temperature so that the same yield can be obtained by reducing the temperature and increasing the catalyst-to-feed ratio or vice versa. Another result showed that the highest selectivity was obtained at the lowest reaction condition of 260 °C. Additionally, it was concluded that 96 wt% of the isomers were multi-branched iso-palmitics. Multi-branched isomers are more effective than mono-branched isomers in minimizing Van Der Waals forces.

Furthermore, not only that the GC-MS & GC-FID did confirm the production of isopalmitics, but they also uncovered the presence of other compounds including linear and cyclic hydrocarbons. Linear compounds were composed of n-pentadecane, n-hexadecane and their isomers that could be used as drop-in biofuel or renewable diesel. Cyclic hydrocarbons were composed of alkyl benzenes, alkyl naphtalenes, and alkyl phenanthrenes. These compounds are applicable as starting materials for a wide range of consumer products such as heat transfer oil and lubricating greases. Production of bioaromatics and long chain alkanes from renewable feedstock, at the same time with

hydroisomerization reaction at moderate process temperatures in turn, could be interpreted as a milestone in this work. This is because compared to the pyrolysis for the production of green fuels, the required temperatures for the hydroisomerization are almost 200 °C lower and as a result, the energy demand is also lower.

Further, based on the experimental results, a novel type of biodiesel plant was designed and simulated by a software known in the chemical industries: Aspen Plus. The novelty of this simulation and design is that this biodiesel plant is modified by the addition of a hydroisomerization unit. Based on the mass and energy balance, a technoeconomic analysis suggested 20 years as the payout period.

Overall, this study successfully targeted a hydroisomerization catalyst, prepared the desired catalyst, designed and performed the experiments, analyzed the samples, and obtained not-only the target compounds to a great extent but also other valueadded materials.

We aware that our research may have three limitations. First, in this research, for hydroisomerization of palmitic acid, limited number of catalyst supports and promoting metals were employed. Second, some of the experiments were carried out in a batch set-up. Third, kinetics of the isomerization was not investigated in this work. Fourth, more advanced separation techniques are other fields that ought to be studied in the future. Thus, for future work the same supports or new supports as reported in chapter 1 promoted with other metallic sites such as palladium or nickel should be examined in continuous systems along with kinetics studies and novel separation techniques.

Despite the above-mentioned barriers, this work produced very promising results not only for biofuels production, but even for biochemicals. Isomers of fatty acids are also used as lubricants, thus there is a wide range of potential applications that could be further evaluated. This study proposed a first milestone to the green chemistry of lipidbased feedstock, and the knowledge generated within this work can be applied to a wide range of upcoming conversion processes for single species molecule of interest for a wide range of applications (chemicals, cosmetics, medicine, transport fuels, etc.).

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