

# Branched fatty acids – the potential of zeolite catalysis

*Dorien Kerstens,<sup>a</sup> Sofie Van Praet,<sup>a</sup> Luca Verhoeven,<sup>b</sup> Pieter Struelens,<sup>b</sup> and Bert F. Sels<sup>a\*</sup>*

<sup>a</sup> Center for Sustainable Catalysis and Engineering, KU Leuven, Celestijnenlaan 200f, 3001  
Leuven, Belgium

<sup>b</sup> Oleon NV, Assenedestraat 2, 9940 Ertvelde, Belgium

## **Corresponding Author**

E-mail address: bert.sels@kuleuven.be

## KEYWORDS

Oleochemistry – Branched fatty acids – Isostearic acid – Isomerization – Zeolites

## ABSTRACT

Isostearic acid, a C18 saturated branched chain fatty acid containing one or more methyl or ethyl groups on the carbon chain, is of great interest for the oleochemical industry due to its interesting physicochemical properties. Its current industrial production, as a side product of the acid clay catalyzed dimerization of unsaturated fatty acids, lacks efficiency. Therefore, research focusses strongly on new catalytic systems based on zeolites. Significantly higher yields of branched fatty acids can be obtained using zeolites, demonstrating their superiority compared to acid clay

catalysts. Despite previous efforts, there is insufficient insight in the product itself and the catalytic system to use it optimally. With this knowledge, it would however be possible to tune zeolite catalysts to meet predetermined product compositions and thus application characteristics. This perspective aims to provide the knowledge required to get a profound insight in the current state-of-the-art while pointing at remaining questions and challenges. Focus is on the reaction mechanisms taking place during reaction, the analysis of the reaction product and the zeolite catalysts themselves.

## INTRODUCTION

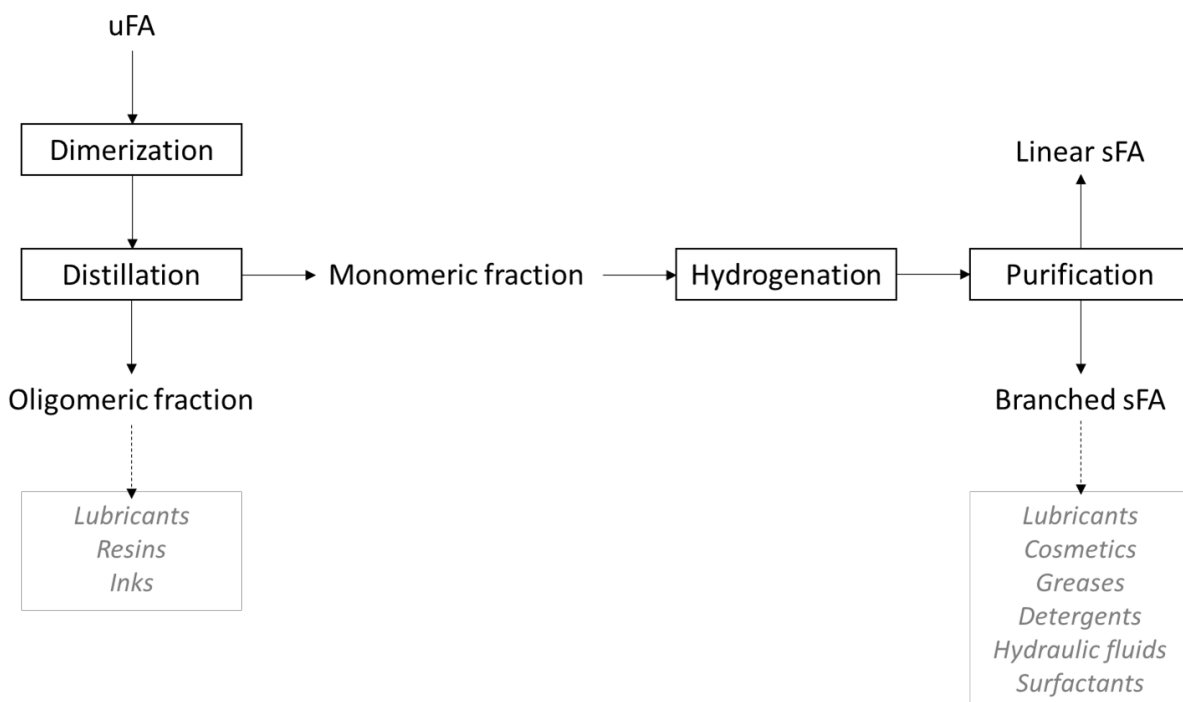
Vegetable and animal oils and fats mainly consist of triacylglycerides, esters of glycerol and three fatty acids. The fatty acids can differ in chain length, degree of saturation and double bond configuration. Most common vegetable oils and fats contain fatty acids, consisting of 16 to 20 carbon atoms and 0 to 3 *cis* double bonds.<sup>1</sup> More than 200 million tons of vegetable and animal oils and fats are produced annually worldwide.<sup>2</sup> About 80 % is used for human nutrition, while 6 % is used in animal feed. The remaining 14 % of these oils and fats are used in the chemical industry, where it is still the most important renewable source of carbon and used for the production of biodiesel and (base) oleochemicals.<sup>3</sup> Therefore, their use comes with some important advantages besides the renewable character, as they are readily available from natural and waste sources, biodegradable and safe to use. Hence, they also fit well in the twelve principles of green chemistry.<sup>4,5</sup>

In the oleochemical industry, the oils and fats are first converted to basic oleochemicals (*i.e.*, free fatty acids, fatty acid methyl esters, glycerol, fatty alcohols and fatty amines) through different

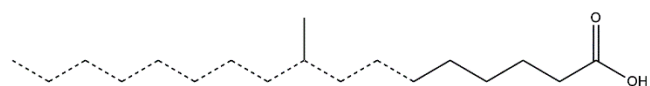
chemical reactions. They are used directly in a wide variety of applications or can be converted to a wide range of specialty chemicals.<sup>6-8</sup>

A significant group of specialty oleochemicals are dimer fatty acids, formed during the dimerization of unsaturated fatty acids such as tall oil fatty acids and, to a lesser extent, oleic acid and linoleic acid. The dimerization can be performed thermally at 270-290 °C, but is typically performed at lower temperatures (190-240 °C) in the presence of an acid clay catalyst such as Bentonite or Montmorillonite. While the thermal oligomerization is believed to be a Diels-Alder type reaction and will not be discussed in further detail, the catalytic oligomerization with acid clays is considered to proceed via multiple mechanisms such as Diels-Alder reaction, radical reaction and Brønsted acid activation of the double bond with the formation of a carbocation intermediate. The charge of this carbocation can shift to different carbon atoms in the chain. Rearrangement of the carbon skeleton can also occur via this carbocation. A complex product mixture is ultimately formed during the dimerization reaction, consisting of a monomeric and an oligomeric fraction, which can be separated utilizing molecular distillation or wiped-film evaporation (**Figure 1**). The oligomeric fraction consists of dimers and higher oligomers such as trimers. The dimers are a complex mixture of cyclic, acyclic, aromatic and bicyclic compounds, which all occur in the form of different isomers (see **Scheme 1** for generalized chemical structures) and are used in a wide variety of products such as lubricants, polyamide resins, epoxy resins and inks. When the dimerization is performed in the presence of an acid clay, the monomeric fraction contains, amongst others, unreacted fatty acids, cyclic fatty acids, lactones and, more importantly, branched fatty acids. These branched fatty acids are formed by rearrangement of the carbocation intermediates and contain one or more methyl or ethyl groups on the carbon chain. After hydrogenation and purification by crystallization, isostearic acid (**Figure 2**) is obtained, which is

a collection of methyl chain-substituted positional isomers of great interest for the oleochemical industry.<sup>7,9-13</sup>

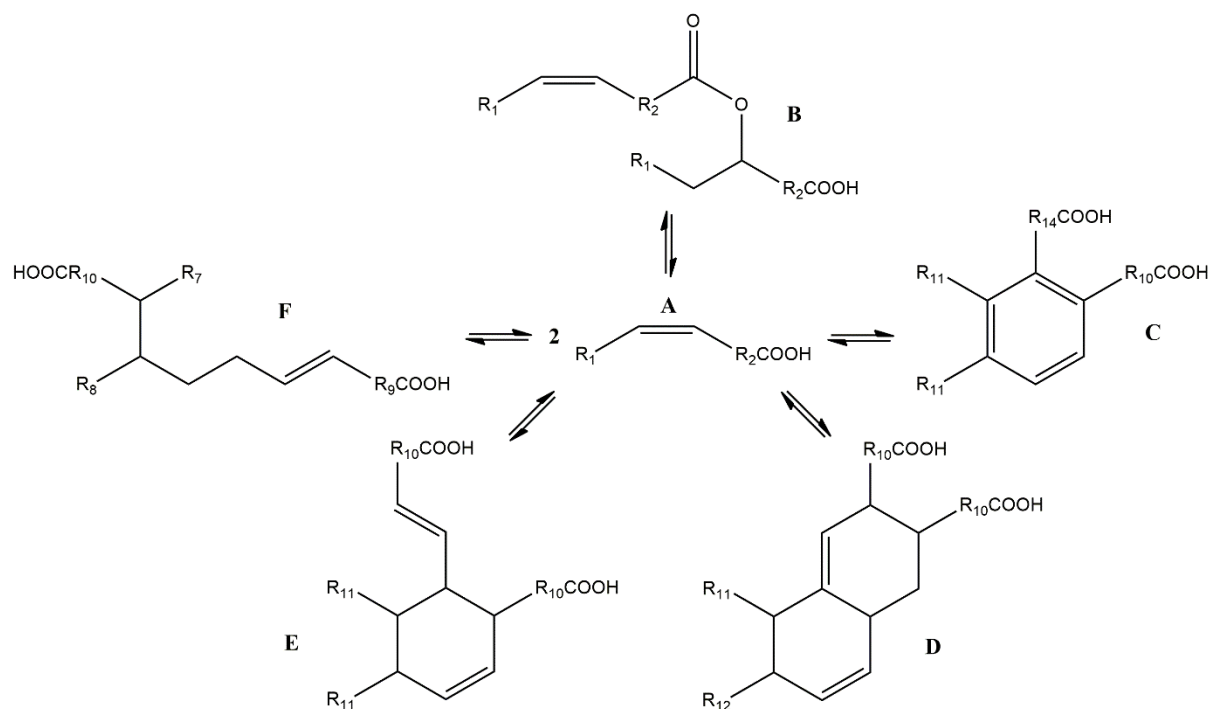


**Figure 1** General overview of the production process of oligomeric acids and isostearic acid from unsaturated fatty acids using acid clays as a catalyst.<sup>10,13,14</sup> Legend: uFA: unsaturated fatty acid; sFA: saturated fatty acid.



**Figure 2** Isostearic acid. The dashed line indicates the possible positions (C6 to C17) of the alkyl branch on the carbon chain.

**Scheme 1** Overview of suggested general chemical structures of fatty acid dimers starting from an unsaturated fatty acid (A). Possible products are estolides (B), aromatic dimers (C), cyclic dimers (D and E) and aliphatic dimers (F).<sup>13</sup>



R<sub>x</sub> indicates a carbon chain with an undefined amount of carbon atoms. When starting from oleic acid as feed, each R<sub>x</sub> with a different x will have a different length.

Given its unique structure, isostearic acid contains some of the most interesting features of both saturated and unsaturated straight-chain fatty acids. As it is free of unsaturations, it is stable against oxidation and can be used in long shelf life or high-temperature applications.<sup>14,15</sup> Because of the presence of one or more methyl (and some ethyl groups) on the carbon chain, it also exhibits low-temperature properties comparable to those of unsaturated fatty acids. Moreover, isostearic acid has a high viscosity index, good biodegradability, and high solubility in organic solvents. As such, isostearic acid is sometimes referred to as ‘the perfect fatty acid’ and is used in several applications such as lubricants (both for high and low-temperature applications) and greases. It is also an essential ingredient in cosmetics and personal care products. Here, the color and odor stability of isostearic acid plays an important role, just like its high solubility in organic solvents.<sup>14-16</sup> Other applications include detergents, surfactants and hydraulic fluids.<sup>14</sup> Despite the many possible

applications of isostearic acid, currently, it is mainly used in demanding applications due to its high cost price.<sup>14,15,17-27</sup> Partly due to a growing cosmetics industry and a rising demand for isostearic acid in the lubricants and greases industry, the compound annual growth rate (CAGR) for the isostearic acid market is now estimated at 5-6 %.<sup>28-30</sup>

Despite the great potential of isostearic acid, the increasing number of applications and the growing global market, it is industrially still produced as a by-product of the dimerization of unsaturated fatty acids. Yields are merely around 25 %, and its purification (consisting of distillation and crystallization as the major steps) is time and energy consuming. Moreover, the clay catalyst cannot be reused and is disposed of after single use.<sup>20,21</sup> Consequently, new processes in which isostearic acid is produced in high yields are thus explored and have been the subject of quite some papers and patents published over the last 25 years. Here, the focus has notably shifted from acid clay to zeolite catalysis, which is considered promising for the selective synthesis of branched fatty acids due to their shape selective properties.<sup>31,32</sup>

This perspective aims to discuss the current state-of-the-art process regarding the production and analysis of branched fatty acids. First, the mechanistic properties of the isomerization of unsaturated fatty acids to branched fatty acids will be tackled. As a result, insight will be gained into which parts of the mechanism are responsible for the isomerization of unsaturated fatty acids to branched fatty acids and what triggers other (parallel and consecutive) side reactions. Secondly, the tools to analyze the complex isomerization product will be discussed. Being able to identify the product distribution accurately is essential since it can be linked to the type of zeolite used. Finally, an overview of the current state-of-the-art regarding zeolite catalysis will be given. Special attention will be paid to the catalytic and structural properties of the zeolites necessary to obtain highly active (and selective) catalysts.

## ISOMERIZATION MECHANISM

As was already briefly mentioned in the introduction, a very complex reaction mixture is obtained during the isomerization reaction, containing both a monomeric and an oligomeric fraction. The desired branched fatty acids are part of the monomeric fraction. All other compounds in the monomeric and oligomeric fractions are considered byproducts and should be avoided if isostearic acid is the target product.

Depending on the Brønsted acid catalyst used, the reaction product often consists of multiple (positional and/or geometrical) isomers, which gives rise to the complex product composition. Moreover, the position of the branch on the carbon chain has an influence on the physicochemical properties of future applications.<sup>14,15</sup> Hence, it epitomizes the importance of thoroughly understanding the reaction mechanism and accurately analyzing the product distribution.

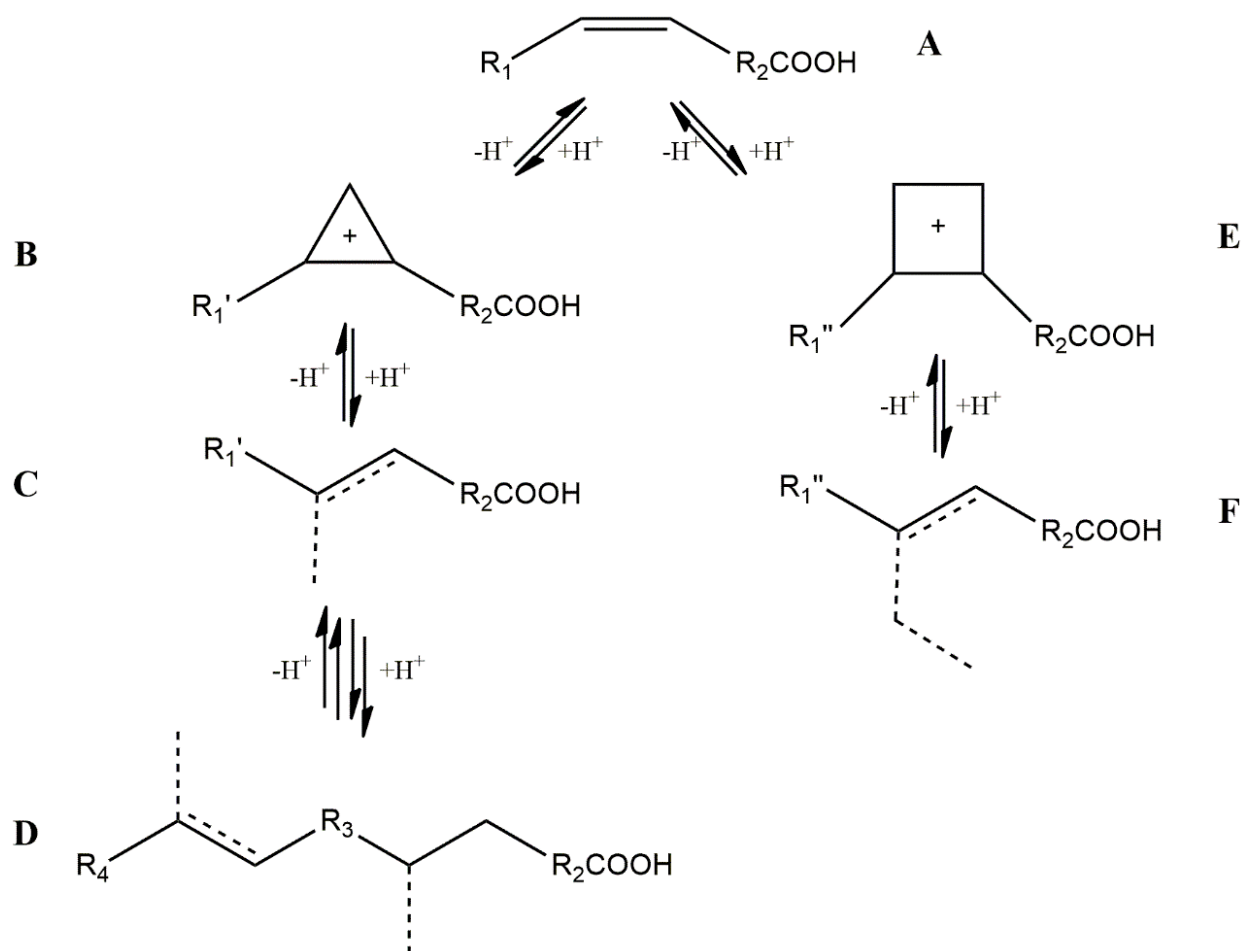
### *MONOMERIC FRACTION*

The complexity of the reaction product is caused by the type of catalysis that takes place during the reaction (**Scheme 2**). A Brønsted acid site will react with the unsaturated fatty acid (A in **Scheme 2**), creating a carbocation. This carbocation has a considerable lifetime at the catalyst's surface and is an intermediate from which a multitude of different products can be formed, but the most important one is the creation of the wanted branched fatty acids. The carbocation, which can be both a three-membered (B in **Scheme 2**) or four-membered ring (E in **Scheme 2**), will lose a proton creating a methyl (C in **Scheme 2**) or ethyl branch (F in **Scheme 2**) on the carbon chain respectively. The unsaturation remains present on the carbon chain and can move along it via the carbocation mechanism, leading to positional isomerization. As such, branches can be formed at several positions, creating multibranching fatty acids (D in **Scheme 2**).<sup>15,20,21,24,33</sup> The dashed lines in **Scheme 2** indicate that according to the movement of the unsaturation on the carbon chain, the

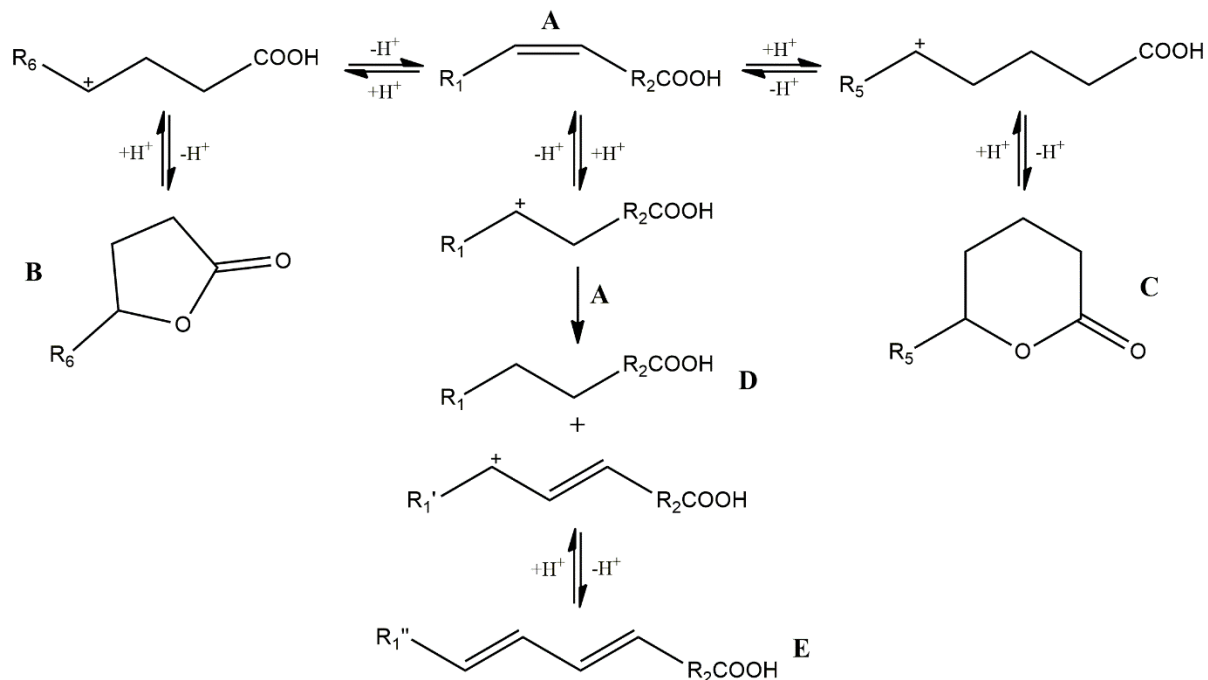
branch and unsaturation can be at any position on the carbon chain, except positions C2 to C5. The unsaturation can be present both in *cis* and *trans* configuration due to the geometrical isomerization of one configuration into the other. However, the *trans* isomer is preferred as it is thermodynamically more stable than the *cis* geometrical isomer.<sup>17,34,35</sup> When a carbocation is formed at position C5 or C4, ring closure will occur by reaction of the carboxyl group with the carbocation, yielding (branched) lactones.<sup>17,20,21,23,24</sup> Both gamma-stearolactone (B in **Scheme 3**) and delta-stearolactone (C in **Scheme 3**) can be formed, but gamma-lactones are thermodynamically favored.<sup>36</sup> However, the presence of (branched) lactones in the reaction product is considered undesired.

**Scheme 2** Proposed reaction mechanism for the skeletal isomerization of unsaturated fatty acids (A) to unsaturated branched chain fatty acids via a three-membered carbocation (B) or four-membered carbocation (E) yielding a methyl branched (C) or ethyl branched (F) unsaturated fatty acid respectively. Monobranched unsaturated fatty acids can be further converted to multibranched unsaturated fatty acids (D).





**Scheme 3** Proposed reaction mechanism for the formation of gamma-lactones (B) and delta-lactones (C), stearic acid (D) and linoleic acid (E) starting from an unsaturated fatty acid (A).<sup>17,38</sup>



R<sub>x</sub><sup>y</sup> indicates a carbon chain with an undefined amount of carbon atoms. When starting from oleic acid as feed, each R<sub>x</sub><sup>y</sup> with a different x or y will have a different length.

The created carbocation takes part in monomolecular reactions and can also react with another unsaturated fatty acid. Via a hydrogen transfer mechanism, two mono-unsaturated fatty acids can be converted into a saturated fatty acid (D in **Scheme 3**) and a double-unsaturated fatty acid (E in **Scheme 3**).<sup>17</sup> The latter does not necessarily have to be a conjugated fatty acid, as different isomers are possibly formed via the carbocation mechanism.

### *OLIGOMERIC FRACTION*

Oligomeric compounds, both dimeric and larger, are formed by the reaction of a fatty acid with another fatty acid or oligomer. While previously mentioned compounds in the monomeric fraction were formed via a carbocation reaction, the formation of oligomers does not necessarily proceed via the same mechanism. Previous research has shown that also radical reactions and Diels-Alder reactions are possible. As such, (depending on the reaction mechanism), multiple dimers and larger

oligomers can be formed, making the product mixture complex regarding its composition. Despite the considerable amount of research performed in the past to elucidate their molecular structures, there is still no certainty or general agreement about it.<sup>13</sup> Moreover, taking into account the complexity of the reaction and, as such, the product's composition, one can understand that a lot of the different monomeric isomers present in the reaction product (*i.e.* branched fatty acids, unsaturated fatty acids) can be incorporated in the dimers and oligomers. On top of that, the dimer itself can further react and undergo isomerization reactions. Consequently, a very heterogeneous intricate mixture of products is created. A more general overview of possible families of dimers is given in **Scheme 1**. On the one side, there are linear dimers that are formed via a carbocation mechanism. A first example is estolides (B in **Scheme 1**), formed via the attack of a carboxyl group of one fatty acid on the carbocation of another fatty acid. As an estolide still contains unsaturation, more fatty acids can be connected to it.<sup>36</sup> A second example is the unsaturated aliphatic dimers (F in **Scheme 1**), formed by the attack of a carbocation of one fatty acid on the double bond of another one.<sup>39-41</sup> On the other side, there is the formation of cyclic (D and E in **Scheme 1**) dimers. For instance, they can be formed via the Diels-Alder reaction of a conjugated unsaturated fatty acid with another unsaturated fatty acid.<sup>40,41</sup> Furthermore, the creation of aromatic dimers (C in **Scheme 1**) is also possible through dehydrogenation steps, which are readily occurring on the (unsaturated) 6 membered ring structures of the intermediates.

## ANALYSIS OF REACTION PRODUCTS

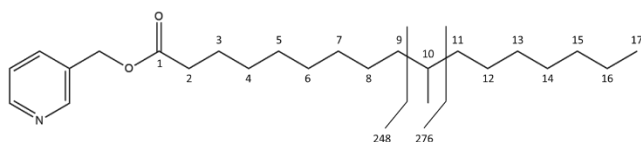
As already stated in the second paragraph, the product obtained after the isomerization of unsaturated fatty acids to unsaturated branched fatty acids is very complex, consisting of a monomeric and oligomeric fraction. Each fraction consists of different chemical compounds present in different isomeric forms. The presence of geometrical and positional isomers of

unsaturated (branched) fatty acids, in particular, causes the compositional analysis to be challenging but necessary. Therefore, reaction products are often hydrogenated before analysis to reduce the number of different compounds present in the raw branched product and facilitate the analysis.<sup>17,22,25,26</sup> A thorough analysis of the reaction products obtained after the isomerization of unsaturated fatty acids to unsaturated branched fatty acids is of the utmost importance. It can also provide more mechanistic insights into the ongoing catalysis and its control of selectivity during the isomerization reaction. As such, one can identify those zeolite characteristics responsible for high yields of the desired product and select/tune zeolites, *e.g.*, through selection or modification of the pore architecture and acidity properties, in such a way that they become more active and selective towards this desired product.

Until now, only more general analysis protocols have been reported to quantify the total amount of branched fatty acids and some byproducts such as lactones, hydroxyl fatty acids and dimers. (HT-)GC and GC-MS analysis are most often used here to quantify both the monomeric and oligomeric fraction.<sup>17,22,25,26</sup> Other techniques, *e.g.* gel permeation chromatography, might be considered as a useful technique for the quantification of the oligomeric fraction. Detailed information about the types of branched fatty acids formed during the reaction is rarely given. Nevertheless, more information on this subject would be interesting, as the position and amount of branches on the carbon chain can influence the physicochemical properties (*e.g.*, phase and melting behavior) of the product and thus also of potential applications or their quality for a specific application.<sup>14,15</sup>

Some progress regarding this subject has been made by the group of Ngo *et al.* The reported analysis is based on derivatizing the fatty acids to 3-pyridylcarbinol ('picolinyl') esters instead of regular fatty acid methyl esters (FAMES). Furthermore, the analysis is performed on a highly polar

Supelco SP-2340 capillary column connected to a mass spectrometer. As picolinyl esters (example given in **Figure 3**) have a very distinct fragmentation pattern on GC-MS, it is possible to determine both the position and type of the branch on the carbon chain. However, the co-elution of some of the picolinyl ester isomers was not prevented during the GC-MS analysis. As such, a large amount of structural information was missing. As a result, the product could only be divided into groups of isomers.<sup>22</sup> To obtain a better separation, Ngo *et al.* opted for a GCxGC-TOF-MS analysis, combining a Restek Dioxin 20 column as the first dimensional column with a Restek PCB column as the second dimensional column. This technique proved that the isomerization of unsaturated fatty acids to unsaturated branched fatty acids with a Ferrierite zeolite results in at least 28 different types of isomers. Moreover, it was demonstrated that Ferrierite's product distribution significantly differed from that of *e.g.* Mordenite. Unfortunately, no details were given about the types of isomers present in the product or any specific differences between the products.<sup>25</sup> As such, there are no clear structural properties/activity – selectivity relationships. The influence of the zeolite on the product distribution of the branched fatty acids was also suggested by Zhang *et al.* It was pointed out that the use of large-pore zeolites results in a relatively large fraction of ethyl-branched fatty acids and multibranching fatty acids. However, no details were given concerning the used analysis protocols.<sup>42</sup>



**Figure 3** 3-pyridylcarbinol ester of 10-methylheptadecanoic acid. Numbers 1 to 17 indicate the different carbon atoms on the carbon chain. A gap will be visible on the mass spectrum between  $m/z$  248 and  $m/z$  275, indicating the position of the methyl branch on carbon 10.

## STATE-OF-THE-ART AND CHALLENGES

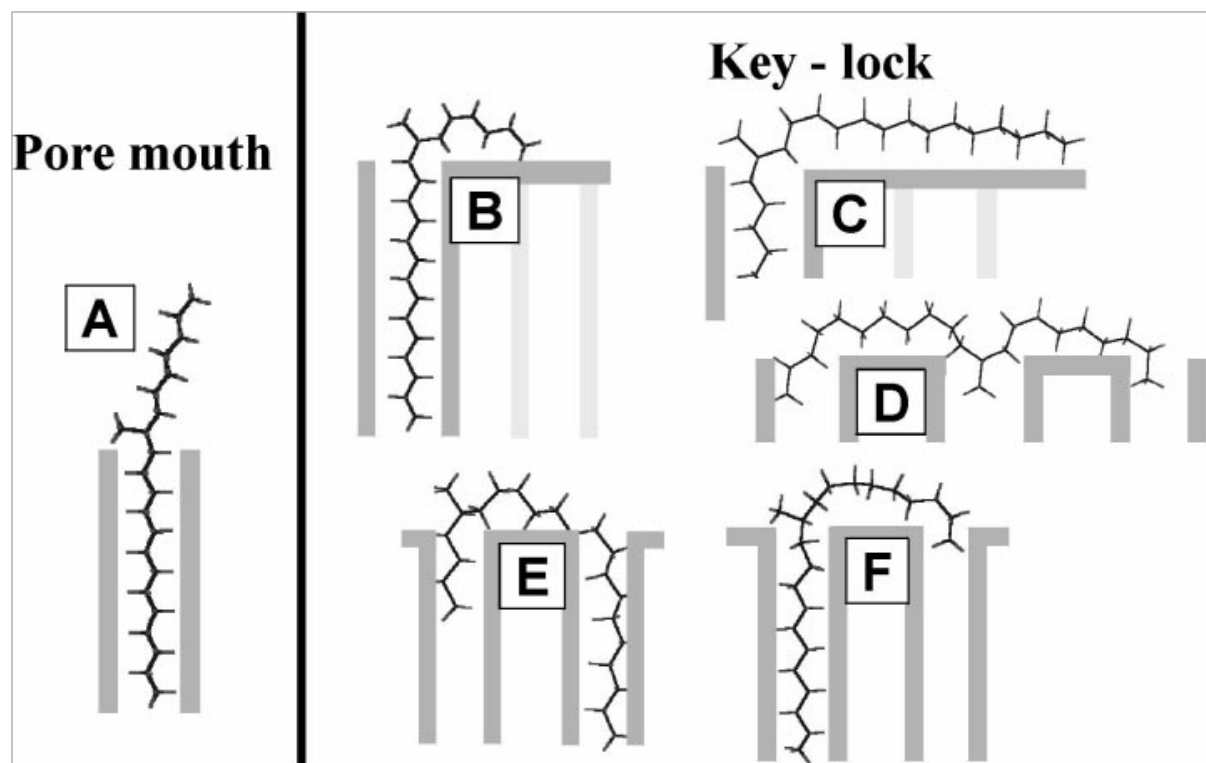
Given the high oleochemical value of branched fatty acids, quite some research on improving the yield has been done since 1980. A proposed adjustment to the clay-catalyzed process is the addition of co-catalysts. Foglia *et al.* use Bentonite in combination with isobutane, said to suppress cracking reactions, and dichloromethane, from which a protonic acid can be generated during the reaction. This method results in a product consisting of 59 wt% branched fatty acids (**Table 1**, entry 1). When these additives are not included, a product consisting of merely 29 % of branched fatty acids is obtained (**Table 1**, entry 2). However, a one-on-one comparison is difficult since different reaction conditions (temperature, duration, catalyst loading) were used. Although higher yields of branched fatty acids can be obtained using clay catalysts, the amount of oligomers in the reaction product remains high. This property is intrinsic to such clay catalysts due to their non-confined catalytically active sites.<sup>43</sup> Therefore, inspired by the selectivity control for the isomerization of olefins and paraffins in the petro-refinery and chemistry business, virtually all recent research focuses on another class of catalysts: zeolites.

Zeolites are crystalline aluminosilicates constructed of  $\text{SiO}_2$  and  $\text{AlO}_4$  tetrahedra connected via shared oxygen atoms. As such, structures with well-defined pores and specific topologies are created. The presence of Al in the framework induces a net negative charge, which has to be compensated by a cation. When this cation is a proton, the zeolite has a Brønsted acidic character.<sup>19,44,45</sup> By using zeolites, it is indeed possible to obtain much higher yields of branched fatty acids. The increased yield can be attributed to their shape selective properties, as a result of the molecular-sized confined space around the active site, retarding/avoiding dimerization. In addition, zeolites are robust and reusable up to 20 times when used to isomerize unsaturated fatty acids to unsaturated branched chain fatty acids.<sup>27</sup>

In the past, zeolites with a more or less accessible microporous structure have been tested as suitable catalysts for the isomerization of unsaturated fatty acids to unsaturated branched chain fatty acids. On the one hand, there are the two-dimensional zeolites, *i.e.* zeolites with a pore network that is accessible for the reagent in two directions of the zeolite crystal. A pore is considered accessible for the reagent - here an unsaturated C18 fatty acid - if it has at least a 10 membered ring (MR) pore. Wiedemann *et al.* have shown that smaller pores, *i.e.* 8 MR pores, do not take part in the isomerization reaction as they are too small.<sup>46</sup> Since the International Zeolite Association (IZA) also includes pores larger than 6 MR in the dimensionality of the zeolite, the dimensionalities mentioned in this perspective can differ from those originally provided by IZA.<sup>47</sup> As a result of the more open structure, two-dimensional zeolites are said to be less prone to deactivation than one-dimensional zeolites (*i.e.* zeolites with a pore network that is accessible for the reagent in only one direction of the zeolite crystal). However, when using these two-dimensional zeolites, such as ZSM-5 (10 MR) and Beta (12 MR), only moderate yields are obtained. When Beta is used, the unsaturated branched chain fatty acid yield is somewhat lower compared to the yield obtained with Bentonite (**Table 1**, entries 6 to 10). With ZSM-5, the obtained yield is somewhat higher than Bentonite, but long reaction times are needed to achieve high conversions (**Table 1**, entry 3).<sup>19,43,48,49</sup> On the other hand, there are one-dimensional zeolites, *i.e.* zeolites with a pore network that is accessible for the reagent in only one direction of the zeolite crystal. When Mordenite (12 MR) is used, a yield of approximately 70 % is achieved (**Table 1**, entries 12 and 13).<sup>50,51</sup> However, most research so far has been performed with Ferrierite (10 MR). This zeolite was considered a very promising catalyst for the first time, already in 2007, by Ngo *et al.* because of its high surface area and high density of Brønsted acid sites.<sup>22</sup> Indeed, with Ferrierite, almost complete feed conversion is possible with high branched fatty acid yields (**Table**

1, entries 14 to 21).<sup>17,22,52</sup> This is not surprising, as Ferrierite is well known for its good performance in the isomerization of hydrocarbons such as *n*-butene.<sup>53,54</sup> Similarly, 10 MR zeolites are known catalysts for the hydroisomerization of *n*-alkanes and are applied in the dewaxing of diesel fractions.<sup>55–59</sup> In this context, bifunctional catalysts are used, consisting of a solid acid support (often a zeolite) and a transition metal in the presence of hydrogen. The latter is used for the dehydrogenation of the *n*-alkane to *n*-alkene, which can then be isomerized via the acid function of the catalyst. Finally, the isomerized alkene is hydrogenated to branched alkane via the metal function of the catalyst. Especially one-dimensional 10 MR zeolites such as ZSM-22 have shown a very specific shape selectivity towards monobranched alkanes. Two theories are suggested to explain these observations: I) pore mouth and key-lock selectivity (PMKLS) and II) the free-energy landscape (FEL) approach.<sup>60</sup> PMKLS suggests that the isomerization of the alkane occurs in the pore mouth of the zeolite, *i.e.* the entrance of the pore at the outer surface of the zeolite. Sorption can occur in one pore mouth, yielding alkanes with a branch at the end of the carbon chain, or, simultaneously in two adjacent pore mouths (key-lock), yielding alkanes with a branch more at the center of the carbon chain or even dibranched isomers (**Figure 4**). This theory works well for zeolites such as ZSM-22 and ZSM-23 (both one-dimensional 10 MR zeolites) performing hydroisomerization reactions on alkanes.<sup>60–62</sup> The FEL approach is used in quantum chemistry, and here the effect of the zeolite structure on thermodynamic characteristics is taken into account. As such, it is assumed that one can predict how the structure of the zeolite will affect its shape selectivity by quantifying how the zeolite topology affects the free energies of formation of reactants, intermediates and products in the zeolite, and this while ignoring the actual chemical characteristics of the zeolite. This theory can be used more widely and is not limited to hydroisomerization reactions with one-dimensional 10 MR zeolites.<sup>60,63</sup>





**Figure 4** Overview of different adsorption configurations (both pore mouth (A) and key-lock (B, C, D, E and F)) on a ZSM-22 zeolite.<sup>61</sup> Reprinted with permission from ref 61. Copyright 2001, Elsevier.

From **Table 1**, it is clear that the use of zeolites for the isomerization of unsaturated fatty acids to unsaturated branched chain fatty acids is often combined with the use of additives. The first commonly used additive is water (when the reagent is a fatty acid) or a lower alcohol (when the reagent is a fatty acid ester). It is assumed that by using water, the activity of the zeolite can be improved due to the modification of Lewis acid sites, *viz.* incompletely coordinated Al sites, to Brønsted acid sites.<sup>17,51,64</sup> However, the benefits of water as an additive with regard to the activity of the zeolite are not very pronounced. In some cases the use of water shows indeed a positive effect on the activity of the zeolite (**Table 1**, entries 7 and 8), whereas in other cases this benefit is insignificant and thus negligible (**Table 1**, entries 3, 4, 14 and 15). Moreover, recent data from

Wiedemann *et al.* and Sarker *et al.* have shown that the presence of water in the reaction mixture promotes the formation of lactones and estolides, both of which are unwanted side products.<sup>17,19</sup> Furthermore, water may also destabilize the zeolite at high hydrothermal conditions by irreversibly destructing the zeolite structure, which is essential to maintain a high selectivity, through desilication or dealumination reactions.<sup>65</sup> This is especially a problem for structurally imperfect zeolite catalysts (as all commercial ones) as well as for zeolites with large pores and low Al content.<sup>66,67</sup> Given pore confinement is at the origin of the high selectivity control, the robustness of the zeolite structure in the reaction is essential. Nevertheless, this point is, for the isomerization conditions of unsaturated fatty acids, until now, not extensively investigated in literature. The second additive that is frequently used, is a bulky Lewis base that binds to the Brønsted acid sites present at the external surface of the zeolite but is too large to enter the pores of the zeolite. As such, the external Brønsted acid sites are neutralized, while the internal ones are still available for catalysis. The aim is to counteract the formation of bulky side products such as dimers, while the formation of monomeric (side) products remains possible in the micropores of the zeolite. Most often, triphenylphosphine (TPP) is used, but other bulky phosphines or amines can be used as well, as long as they cannot enter the micropores of the zeolite. Different research groups have shown that the presence of TPP in the reaction mixture indeed has a positive effect on the selectivity of the zeolite, as the amount of oligomers present in the reaction product reduces significantly. However, the presence of these bulky Lewis bases can have a negative effect on the activity of the zeolite, depending on the reaction conditions used (**Table 1**, entries 4, 5, 8, 9, 16 to 21).<sup>16–18,52,68,69</sup> This effect is attributed to the blockage of the pore mouths of the zeolite. As such, the catalytically active sites are not sufficiently accessible for the isomerization reaction.<sup>13</sup> In analogy with the hydroisomerization of *n*-alkanes with zeolites, the catalytic conversion of unsaturated fatty acids

to unsaturated branched chain fatty acids is also believed to occur in the pore mouths of the zeolite and not within the microporous network itself. This finding was suggested for the first time by Wiedemann *et al.*, who looked in more detail at the deactivation mechanisms during a reaction with Ferrierite in the presence of water and TPP. It was observed that deactivation of the Ferrierite zeolite is likely to occur via two distinct mechanisms. The first one is the strong adsorption of polyenylic species, formed via hydrogen transfer mechanisms, on the acid sites in the pore mouths of the zeolite. As such, the isomerization reaction is slowed down.<sup>17,70</sup> The second one is linked to the formation of cokes in the zeolite pores. Wiedemann *et al.* have shown that the pores of the Ferrierite zeolite get blocked very early in the reaction by the formation of cokes. The amount of cokes present in the zeolite crystals remains more or less constant during the reaction. As such, the reaction cannot take place (largely) inside the micropores of the zeolite. They reasoned that, as TPP was also present in the reaction mixture and blocked the acid sites on the zeolite's surface, the reaction could only take place in the pore mouths of the zeolite.<sup>17,46,70</sup> As stated earlier, it is not surprising that pore mouth catalysis is suggested for this type of reaction, as it was already suggested by Martens *et al.* for the hydroisomerization of long *n*-alkanes with one-dimensional 10 MR zeolites, such as ZSM-22.<sup>59,61,62,71</sup> Specifically for Ferrierite, pore mouth catalysis has been suggested for the isomerization of *n*-butene.<sup>72,73</sup> Nevertheless, more research is necessary to confirm that the isomerization of fatty acids with 10 MR zeolites also takes place via pore mouth catalysis, given that the adsorption of fatty acids may behave differently due to their bipolar structure with a polar head and nonpolar tail.

The zeolite characteristics responsible for a high activity and selectivity towards branched fatty acids are not fully elucidated. Wiedemann *et al.* found that the initial activity of Ferrierite, shown as the conversion after 8 minutes, correlates well with the number of Brønsted acid sites present

in the 10 MR pores, measured with pyridine IR. High yields of branched fatty acids can be explained by the high ratio of Brønsted to Lewis acid sites.<sup>70</sup> Ha *et al.*, who tested different Beta zeolites calcined at different temperatures, also mention the relationship between high Brønsted acidity and high activity.<sup>24</sup> Zhang *et al.*, in contrast, claim that not only the Si/Al ratio is an essential measure for a zeolite's activity, as it correlates to its acidity, but also the accessibility of the acid sites for the reagent. For the first time, a mesoporous zeolite (MAS-5) was used. MAS-5 is a zeolite with mesopores between 15 and 500 Å consisting of primary and secondary nano-sized zeolite structural units in the walls of the mesopores. These structural units consist of microporous Beta zeolite, giving the zeolite the advantages of both a microporous and a mesoporous zeolite as it has an acidity and thermal and hydrothermal stability comparable to conventional, microporous zeolites. Additionally, by introducing mesopores in a zeolite, the substrate and product can diffuse in and out the zeolite more easily, which should give rise to a higher catalytic activity. When compared to a Beta zeolite with a similar Si/Al ratio, one can see that the presence of mesopores indeed positively influences the activity of the zeolite (**Table 1** entries 10 and 11).<sup>21,74</sup> In contrast, the most active Beta zeolite in the work of Ha *et al.* has a relatively low surface area.<sup>24</sup> Zeolites such as the MAS-5 are considered hierarchical zeolites, *i.e.* zeolites that contain, on top of and interconnected with a microporous pore network, a pore network consisting of meso- and/or macropores. They can be obtained via different methods, both during zeolite synthesis (*i.e.* via bottom-up methods) or after zeolite synthesis (*i.e.* via top-down methods) and have proven to show an improved catalytic performance compared to microporous zeolites in many applications.<sup>44</sup> The use of hierarchical zeolites for the isomerization of unsaturated fatty acids to unsaturated branched chain fatty acids is still very limited as next to Zhang *et al.*, only Bolshakov *et al.* recently looked into it. They used a bottom-up synthesized hierarchical Ferrierite and compared it to a reference,

non-hierarchical, Ferrierite. Due to the presence of the hierarchical pore system, higher yields of branched fatty acids were obtained, which was attributed to an improved mass transport. The influence of mesoporosity on the mono *versus* multi branching ratio or other impacts on the isomerization selectivity were unfortunately not reported.<sup>75</sup>

**Table 1** Overview of patents and journal papers concerning the branching of unsaturated fatty acids.

Entry	Catalyst	Si / Al	Loading (wt% on feed)	Substrate	Additives (wt% on feed)	Temperature (°C)	Time (h)	BFA' s (wt%)	X (%)	Y (%)	S (%)	Ref.
1	Bentonite	—	10	Methyl oleate	Isobutane (60), 1,2-dichloroethane (200)	230	2	59	—	—	—	43
2	Bentonite	—	5	Methyl oleate	—	250	24	29	—	—	—	43
3	H-ZSM-5	11.5	5	Oleic acid	—	260	24	65	98	—	—	19
4	H-ZSM-5	11.5	5	Oleic acid	Water (2)	260	24	68	100	—	—	19
5	H-ZSM-5	11.5	5	Oleic acid	Water (2), TPP (0.375)	260	24	80	98	—	—	19
6	H-Beta	50	10	Oleic acid	—	250	7	46	74	59	79	49
7	H-Beta	12.5	5	Oleic acid	—	260	4	43	79	—	—	19
8	H-Beta	12.5	5	Oleic acid	Water (3.6)	260	4	53	89	—	—	19
9	H-Beta	12.5	5	Oleic acid	Water (3.6), TPP (0.375)	260	4	41	70	—	—	19
10	H-Beta	25	10	Oleic acid	—	250	5	—	49	—	—	74

11	H-MAS-5	25	10	Oleic acid	—	25 0	5	31	6 0	—	74
12	H-Mordenite	6.5	5	Oleic acid	—	26 5	4	—	—	68	51
13	H-Mordenite	7	8	Oleic acid	Water (2)	28 0	6	—	—	71	64
14	H-Fer	10	5	Oleic acid	—	26 0	8	74	9 9	—	19
15	H-Fer	10	5	Oleic acid	Water (3.6)	26 0	8	73	1 0 0	—	19
16	H-Fer	9	5	Oleic acid	Water (3.6), TPP (0.125)	25 0	6	48	7 2	—	52
17	H-Fer	9	5	Oleic acid	Water (3.6), TPP (0.125)	25 0	22	77	9 9	—	52
18	H-Fer	9	5	Oleic acid	Water (3.6)	28 0	6	67	9 9	—	52
19	H-Fer	9	5	Oleic acid	Water (3.6), TPP (0.5)	28 0	6	79	9 8	—	52
20	H-Fer	9	5	Oleic acid	Water (1)	26 0	6	62	9 5	67	70 17
21	H-Fer	9	5	Oleic acid	Water (1), TPP (0.375)	26 0	6	75	9 2	81	88 17

Legend: BFA's: branched fatty acids; X: conversion; Y: yield; S: selectivity; TPP: triphenylphosphine.

## CONCLUSIONS

Due to their unique properties, branched fatty acids are of great interest to the oleochemical industry. However, their current industrial production is limited and only as a side product of the acid clay catalyzed dimerization of fatty acids. Yields are low, and purification is very energy-consuming. Hence, efforts were made to increase their yields, mainly relying on zeolites as a catalyst. As such, important steps forward were made, but a considerable amount of questions

remain open. This perspective aims to provide all the knowledge required to get a profound insight in the current state-of-the-art while pointing at these remaining questions.

Despite the efforts of some research groups, additional improvements are required concerning the analysis of the reaction product. Due to the type of chemistry taking place, *i.e.* carbocation chemistry, the product is extremely complex and consists of a high amount of isomers, both in the fraction of branched fatty acids as in the fraction of unwanted side products. A deepened knowledge here would create a better understanding between a product's composition and its physicochemical properties.

The use of zeolite catalysts has made it possible to tremendously increase the yield of branched fatty acids, compared to the current industrial process. While it was already pointed out in literature that different zeolites give different product compositions, and thus that its activity and selectivity strongly depends on the characteristics of the zeolite, the reason for this remains unclear due to the lack of available detailed (molecular) information about these differences. Nevertheless, more detailed insights in the reaction products could help researchers to understand how the zeolite catalyst is capable of improving *e.g.* selectivity. Proper knowledge on this matter, combined with a more detailed product analysis, would make it possible to design application-specific catalytic systems.

Clearly, plenty opportunities are still ahead, not only regarding the analysis of the reaction products but also with regard to further improving the catalytic system. The focus here should be on developing additive-free, robust catalytic systems yielding high amounts of branched fatty acids under moderate reaction conditions, which can act as a sustainable alternative for the currently used acid clays. It might also be interesting to look at cheaper zeolite systems of greater industrial interest than the currently used Ferrierite or at continuous reaction systems such as fixed bed or

continuous stirred tank reactors, as current research is almost exclusively performed on batch systems. A thorough and systematic insight into the relationship between activity/selectivity and zeolite characteristics will be essential here. It will make it possible to tune the catalytic system towards the desired yields and product properties. Finally, improved insights into the deactivation mechanisms during reaction will make it possible to develop more robust zeolites and tailor-made regeneration protocols, free of additives and suited for industrial applications.

#### AUTHOR INFORMATION

##### **Corresponding Author**

E-mail address: bert.sels@kuleuven.be

#### ACKNOWLEDGMENT

D.K. acknowledges Flanders Innovation & Entrepreneurship (VLAIO) for financial support (HBC.2017.1014).

#### REFERENCES

- (1) Philippaerts, A.; Paulussen, S.; Breesch, A.; Turner, S.; Lebedev, O. I.; Tendeloo, G. Van; Sels, B.; Jacobs, P. Unprecedented Shape Selectivity in Hydrogenation of Triacylglycerol Molecules with Pt / ZSM-5 Zeolite. *Angew. Chemie - Int. Ed.* **2011**, *50*, 3947–3949. <https://doi.org/10.1002/anie.201007513>.
- (2) R.E.A. Holdings PLC. World production of oils and fats <http://www.rea.co.uk/markets/oils-fats/world-production-oils-fats> (accessed Jul 4, 2018).
- (3) Metzger, J. O.; Meier, M. A. R. Fats and Oils as Renewable Feedstock for the Chemical Industry. *Eur. J. Lipid Sci. Technol.* **2011**, *113* (1), 1–2.



<https://doi.org/10.1002/ejlt.201500535>.

- (4) Salimon, J.; Salih, N.; Yousif, E. Industrial Development and Applications of Plant Oils and Their Biobased Oleochemicals. *Arab. J. Chem.* **2012**, *5* (2), 135–145. <https://doi.org/10.1016/j.arabjc.2010.08.007>.
- (5) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press, 1998.
- (6) Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. Oils and Fats as Renewable Raw Materials in Chemistry. *Angew. Chemie Int. Ed.* **2011**, *50* (17), 3854–3871. <https://doi.org/10.1002/anie.201002767>.
- (7) Rebsdatt, S.; Mayer, D. Fatty Acids. *Ullmann's Encyclopedia of Industrial Chemistry*; 2012; pp 73–116. <https://doi.org/10.1002/14356007.a10>.
- (8) Behr, A.; Westfechtel, A.; Pérez Gomes, J. Catalytic Processes for the Technical Use of Natural Fats and Oils. *Chem. Eng. Technol.* **2008**, *31* (5), 700–714. <https://doi.org/10.1002/ceat.200800035>.
- (9) Koster, R. Solid Acid Catalysed Conversions of Oleochemicals. Ph.D. Thesis, University of Amsterdam, The Netherlands, 2003.
- (10) Breuer, T. E. Dimer Acids. *Kirk-Othmer Encyclopedia of Chemical Technology*; 2000. <https://doi.org/10.1007/BF02672546>.
- (11) Cornils, B.; Lappe, P. Dicarboxylic Acids, Aliphatic. *Ullmann's Encyclopedia of Industrial Chemistry*; 2014. [https://doi.org/doi:10.1002/14356007.a08\\_523.pub3](https://doi.org/doi:10.1002/14356007.a08_523.pub3).

- (12) Sublett, M.; Blewitt, W. C. Process for producing light color dimer acids from the dimerization of unsaturated fatty acids. WO 00/75252 A1, 2000.
- (13) Zhang, J.; Nuñez, A.; Strahan, G. D.; Ashby, R.; Huang, K.; Moreau, R. A.; Yan, Z.; Chen, L.; Ngo, H. An Advanced Process for Producing Structurally Selective Dimer Acids to Meet New Industrial Uses. *Ind. Crops Prod.* **2020**, *146*, 112132. <https://doi.org/10.1016/j.indcrop.2020.112132>.
- (14) Wiedemann, S. C. C.; Bruijninx, P. C. A.; Weckhuysen, B. M. Isostearic Acid: A Unique Fatty Acid with Great Potential. In *Chemicals and Fuels from Bio-Based Building Blocks*; Cavani, F., Albonetti, S., Basile, F., Gandini, A., Eds.; 2016; pp 51–78. <https://doi.org/10.1002/9783527698202.ch3>.
- (15) Hasselberg, J.; Behr, A. Saturated Branched Fatty Compounds : Proven Industrial Processes and New Alternatives. *Eur. J. Lipid Sci. Technol.* **2016**, *118*, 36–46. <https://doi.org/10.1002/ejlt.201500461>.
- (16) Sarker, M. I.; Moreau, R. A.; Ngo, H. Comparison of Various Phosphine Additives in Zeolite Based Catalytic Isomerization of Oleic Acid. *Eur. J. Lipid Sci. Technol.* **2018**, *120* (6), 1800070. <https://doi.org/10.1002/ejlt.201800070>.
- (17) Wiedemann, S. C. C.; Stewart, J. A.; Soulimani, F.; Bergen-brenkman, T. Van; Langelaar, S.; Wels, B.; Peinder, P. De; Bruijninx, P. C. A.; Weckhuysen, B. M. Skeletal Isomerisation of Oleic Acid over Ferrierite in the Presence and Absence of Triphenylphosphine: Pore Mouth Catalysis and Related Deactivation Mechanisms. *J. Catal.* **2014**, *316*, 24–35. <https://doi.org/10.1016/j.jcat.2014.04.018>.

- (18) Ngo, H. L. Lewis Base Additives Improve the Zeolite Ferrierite - Catalyzed Synthesis of Isostearic Acids. *J. Am. Oil Chem. Soc.* **2015**, *92*, 613–619. <https://doi.org/10.1007/s11746-015-2608-5>.
- (19) Sarker, M. I.; Latona, R. J.; Moreau, R. A.; Micheroni, D.; Jones, K. C.; Ngo, H. Convenient and Environmentally Friendly Production of Isostearic Acid with Protonic Forms of Ammonium Cationic Zeolites. *Eur. J. Lipid Sci. Technol.* **2017**, *119* (12), 1–8. <https://doi.org/10.1002/ejlt.201700262>.
- (20) Zhang, Z. C.; Dery, M.; Zhang, S.; Steichen, D. New Process for the Production of Branched-Chain Fatty Acids. *J. Surfactants Deterg.* **2004**, *7* (3), 211–215.
- (21) Zhang, S.; Zhang, Z. C. Skeletal Isomerization of Unsaturated Fatty Acids : The Role of Mesopores in HBeta Zeolites. *Catal. Letters* **2007**, *115* (3–4), 114–121. <https://doi.org/10.1007/s10562-007-9083-z>.
- (22) Ngo, H. L.; Nuñez, A.; Lin, W.; Foglia, T. A. Zeolite-Catalyzed Isomerization of Oleic Acid to Branched-Chain Isomers. *Eur. J. Lipid Sci. Technol.* **2007**, *108*, 214–224. <https://doi.org/10.1002/ejlt.200600246>.
- (23) Biermann, U.; Metzger, J. O. Synthesis of Alkyl-Branched Fatty Acids. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 805–811. <https://doi.org/10.1002/ejlt.200800033>.
- (24) Ha, L.; Mao, J.; Zhou, J.; Zhang, Z. C.; Zhang, S. Skeletal Isomerization of Unsaturated Fatty Acids on Beta Zeolites : Effects of Calcination Temperature and Additives. *Appl. Catal. A Gen.* **2009**, *356*, 52–56. <https://doi.org/10.1016/j.apcata.2008.12.018>.
- (25) Ngo, H. L.; Hoh, E.; Foglia, T. A. Improved Synthesis and Characterization of Saturated

- Branched-Chain Fatty Acid Isomers. *Eur. J. Lipid Sci. Technol.* **2012**, *114*, 213–221.  
<https://doi.org/10.1002/ejlt.201000471>.
- (26) Ngo, H. L.; Dunn, R. O.; Hoh, E. C18-Unsaturated Branched-Chain Fatty Acid Isomers : Characterization and Physical Properties. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 676–683.  
<https://doi.org/10.1002/ejlt.201200323>.
- (27) Ngo, H. L. Improved Zeolite Regeneration Processes for Preparing Saturated Branched - Chain Fatty Acids. *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 645–652.  
<https://doi.org/10.1002/ejlt.201300315>.
- (28) Research, A. M. *Global Isostearic Acid Market Size, Market Share, Application Analysis, Regional Outlook, Growth Trends, Key Players, Competitive Strategies And Forecasts, 2017 To 2025*; 2017.
- (29) Research, P. M. *Global Isostearic Acid Market Size, Share, Development, Growth and Demand Forecast to 2020 – Industry Insights by End-User (Chemical Esters, Personal Care, Lubricants and Greases, and Others)*; 2015.
- (30) Research, Z. M. *Global Isostearic Acid Market Will Reach USD 920 Million by 2025: Zion Market Research*; 2018.
- (31) Ennaert, T.; Van Aelst, J.; Dijkmans, J.; De Clercq, R.; Schutyser, W.; Dusselier, M.; Verboekend, D.; Sels, B. F. Potential and Challenges of Zeolite Chemistry in the Catalytic Conversion of Biomass. *Chem. Soc. Rev.* **2016**, *45* (3), 584–611.  
<https://doi.org/10.1039/c5cs00859j>.
- (32) Sastre, G.; Corma, A. The Confinement Effect in Zeolites. *J. Mol. Catal. A Chem.* **2009**,

- 305, 3–7. <https://doi.org/10.1016/j.molcata.2008.10.042>.
- (33) Reaume, S. J.; Ellis, N. Optimizing Reaction Conditions for the Isomerization of Fatty Acids and Fatty Acid Methyl Esters to Their Branch Chain Products. *J. Am. Oil Chem. Soc.* **2011**, *88*, 661–671. <https://doi.org/10.1007/s11746-010-1718-3>.
- (34) Reaume, S. J.; Ellis, N. Synergistic Effects of Skeletal Isomerization on Oleic and Palmitic Acid Mixtures for the Reduction in Cloud Point of Their Methyl Esters. *Energy & Fuels* **2012**, *26*, 4514–4520.
- (35) den Otter, M. J. A. M. The Dimerization of Oleic Acid with a Montmorillonite Catalyst II: GLC Analysis of the Monomer; the Structure of the Dimer; a Reaction Model. *Fette Seifen Anstrichm.* **1970**, *10*, 875–883.
- (36) Cermak, S. C.; Isbell, T. A. Synthesis of  $\delta$ -Stearolactone from Oleic Acid. *J. Am. Oil Chem. Soc.* **2000**, *77* (3), 243–248. <https://doi.org/10.1007/s11746-000-0040-6>.
- (37) Link, W.; Spitteller, G. Produkte Der Dimerisierung Ungesättigter Fettsäuren I: Die Monomerfraktion Der Dimerisierung Reiner Ölsäure. *Fat Sci. Technol.* **1990**, *92*, 19–25.
- (38) Isbell, T. A.; Kleiman, R. Mineral Acid-Catalyzed Condensation of Meadowfoam Fatty Acids into Estolides. *J. Am. Oil Chem. Soc.* **1996**, *73* (9), 1097–1107. <https://doi.org/10.1007/BF02523369>.
- (39) Ionescu, M.; Petrovic, Z. S. Polymerization of Soybean Oil with Superacids. In *Soybean - Applications and Technology*; Ng, T.-B., Ed.; 2011; pp 365–386. <https://doi.org/10.5772/621>.
- (40) Huang, X.; Yin, Y.; Zhang, B.; Feng, G. Effects of the Structure and Composition of

- Montmorillonite on the Dimerization of Unsaturated Fatty Acids. *J. Braz. Chem. Soc.* **2018**, *29* (7), 1516–1526.
- (41) Tolvanen, P.; Mäki-Arvela, P.; Kumar, N.; Eränen, K.; Sjöholm, R.; Hemming, J.; Holmbom, B.; Salmi, T.; Murzin, D. Y. Thermal and Catalytic Oligomerisation of Fatty Acids. *Appl. Catal. A Gen.* **2007**, *330* (1–2), 1–11. <https://doi.org/10.1016/j.apcata.2007.06.012>.
- (42) Zhang, Z. C.; Dery, M.; Zhang, S.; Steichen, D. New Process for the Production of Branched-Chain Fatty Acids. *J. Surfactants Deterg.* **2004**, *7* (3), 211–215. <https://doi.org/10.1007/s11743-004-0306-x>.
- (43) Foglia, T. A.; Perlstein, T.; Nakano, Y.; Maerker, G. Process for the Preparation of Branched Chain Fatty Acids and Esters. US 4,371,469, 1983.
- (44) Kerstens, D.; Smeyers, B.; Van Waeyenberg, J.; Zhang, Q.; Yu, J.; Sels, B. F. State of the Art and Perspectives of Hierarchical Zeolites: Practical Overview of Synthesis Methods and Use in Catalysis. *Adv. Mater.* **2020**, *32* (44). <https://doi.org/10.1002/adma.202004690>.
- (45) Zhang, S.; Zhang, Z. fatty acid isomerization with mesoporous zeolites. US2003191331A1, 2003
- (46) Wiedemann, S. C. C.; Ristanovic, Z.; Whiting, G. T.; Reddy Marthala, V. R.; Kärger, J.; Weitkamp, J.; Wels, B.; Bruijninx, P. C. A.; Weckhuysen, B. M. Large Ferrierite Crystals as Models for Catalyst Deactivation during Skeletal Isomerisation of Oleic Acid: Evidence for Pore Mouth Catalysis. *Chem. - A Eur. J.* **2016**, *22* (1), 199–210. <https://doi.org/10.1002/chem.201503551>.

- (47) Association, S. C. of the I. Z. Database of zeolite structures <http://www.iza-structure.org/databases/> (accessed November 2021).
- (48) Zhang, S.; Zhang, Z.; Steichen, D. Skeletal Isomerization of Alkyl Esters and Derivatives Prepared Therefrom. US 2003/0191330 A1, 2003.
- (49) Zhang, Z.; Zhang, S.; Steichen, D. Skeletal Isomerization of Fatty Acids. US 6,831,184 B2, 2004.
- (50) Tomifuji, T.; Abe, H.; Matsumura, Y.; Sakuma, Y. EP 0 683 150 B1, 1995.
- (51) Hodgson, W. R.; Lok, C. M.; Roberts, G.; Koetsier, W. T. Fatty Acid Isomerisation. EP 0 774 451 A1, 1997.
- (52) Ngo, H. L.; Hoh, E.; Foglia, T. A. Improved Synthesis and Characterization of Saturated Branched-Chain Fatty Acid Isomers. *Eur. J. Lipid Sci. Technol.* **2012**, *114* (2), 213–221. <https://doi.org/10.1002/ejlt.201000471>.
- (53) Jo, D.; Hong, S. B.; Cambor, M. A. Monomolecular Skeletal Isomerization of 1-Butene over Selective Zeolite Catalysts. *ACS Catal.* **2015**, *5* (4), 2270–2274. <https://doi.org/10.1021/acscatal.5b00195>.
- (54) Kim, W.; Kim, J.; Ahn, B. J.; Seo, G. The Skeletal Isomerization of C4-C7 1-Olefins over Ferrierite and ZSM-5 Zeolite Catalysts. *Korean J. Chem. Eng.* **2001**, *18* (1), 120–126.
- (55) Bouchy, C.; Hastoy, G.; Guillon, E.; Martens, J. A. Fischer-Tropsch Waxes Upgrading via Hydrocracking and Selective Hydroisomerization. **2009**, *64* (1), 91–112. <https://doi.org/10.2516/ogst/2008047>.

- (56) Zhang, M.; Chen, Y.; Wang, L.; Zhang, Q.; Tsang, C. W.; Liang, C. Shape Selectivity in Hydroisomerization of Hexadecane over Pt Supported on 10-Ring Zeolites: ZSM-22, ZSM-23, ZSM-35, and ZSM-48. *Ind. Eng. Chem. Res.* **2016**, *55* (21). <https://doi.org/10.1021/acs.iecr.6b01163>.
- (57) Miller, S. J. New Molecular Sieve Process for Lube Dewaxing by Wax Isomerization. *Microporous Mater.* **1994**, *2* (5), 439–449. [https://doi.org/10.1016/0927-6513\(94\)00016-6](https://doi.org/10.1016/0927-6513(94)00016-6).
- (58) Nghiem, V. T.; Sapaly, G.; Mériaudeau, P.; Naccache, C. Monodimensional Tubular Medium Pore Molecular Sieves for Selective Hydroisomerisation of Long Chain Alkanes: N-Octane Reaction on ZSM and SAPO Type Catalysts. *Top. Catal.* **2000**, *14* (1–4), 131–138. <https://doi.org/10.1023/A:1009071403372>.
- (59) Mäki-Arvela, P.; Khel, T. A. K.; Azkaar, M.; Engblom, S.; Murzin, D. Y. Catalytic Hydroisomerization of Long-Chain Hydrocarbons for the Production of Fuels. *Catalysts* **2018**, *8* (11), 534. <https://doi.org/10.3390/catal8110534>.
- (60) Gerasimov, D. N.; Fadeev, V. V.; Loginova, A. N.; Lysenko, S. V. Hydroisomerization of Long Chain Paraffins: Mechanism and Catalysts . Part I. **2015**, *7* (2), 128–154. <https://doi.org/10.1134/S2070050415020051>.
- (61) Martens, J. A.; Vanbutsele, G.; Jacobs, P. A.; Denayer, J.; Ocakoglu, R.; Baron, G.; Arroyo, J. A. M.; Thybaut, J.; Marin, G. B. Evidences for Pore Mouth and Key – Lock Catalysis in Hydroisomerization of Long n -Alkanes over 10-Ring Tubular Pore Bifunctional Zeolites. *Catal. Today* **2001**, *65*, 111–116.
- (62) Claude, M. C.; Martens, J. A. Monomethyl-Branching of Long n-Alkanes in the Range from



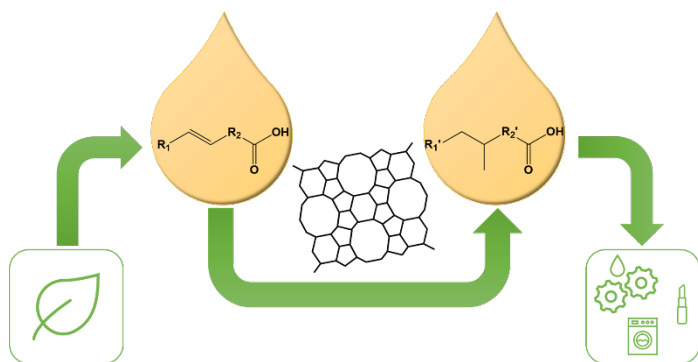
- Decane to Tetracosane on Pt / H-ZSM-22 Bifunctional Catalyst. **2000**, *48*, 39–48.  
<https://doi.org/10.1006/jcat.1999.2714>.
- (63) Smit, B.; Maesen, T. L. M. Towards a Molecular Understanding of Shape Selectivity. *Nature* **2008**, *451* (7179), 671–678. <https://doi.org/10.1038/nature06552>.
- (64) Tomifuji, T.; Abe, H.; Matsumura, Y.; Sakuma, Y. Process for the Preparation of Branched Chain Fatty Acids and Alkyl Esters Thereof. EP 0 683 150 A1, 1995.
- (65) Heard, C. J.; Grajciar, L.; Uhlík, F.; Shamzhy, M.; Opanasenko, M.; Čejka, J.; Nachtigall, P. Zeolite (In)Stability under Aqueous or Steaming Conditions. *Adv. Mater.* **2020**, *32* (44).  
<https://doi.org/10.1002/adma.202003264>.
- (66) Ennaert, T.; Geboers, J.; Gobechiya, E.; Courtin, C. M.; Kurttepli, M.; Houthoofd, K.; Kirschhock, C. E. A.; Magusin, P. C. M. M.; Bals, S.; Jacobs, P. A.; Sels, B. F. Conceptual Frame Rationalizing the Self-Stabilization of H-USY Zeolites in Hot Liquid Water. *ACS Catal.* **2015**, *5*, 754–768. <https://doi.org/10.1021/cs501559s>.
- (67) Zhang, L.; Chen, K.; Chen, B.; Resasco, D. E. Factors That Determine Zeolite Stability in Hot Liquid Water. *J. Am. Chem. Soc.* **2015**, *137*, 11810–11819.  
<https://doi.org/10.1021/jacs.5b07398>.
- (68) Fan, M.; Si, T.; Zhang, P. Effect of Surface Modification of H<sup>+</sup>-Mordenite on the Isomerization of Oleic Acid into Branched-Chain Isomers. *JAACS, J. Am. Oil Chem. Soc.* **2018**, *95* (11), 1357–1365. <https://doi.org/10.1002/aocs.12142>.
- (69) Zhang, J.; Uknalis, J.; Chen, L.; Moreau, R. A.; Ngo, H. Development of Magnesium Oxide–Zeolite Catalysts for Isomerization of Fatty Acids. *Catal. Letters* **2019**, *149*, 303–

312. <https://doi.org/10.1007/s10562-018-2601-3>.
- (70) Wiedemann, S. C. C.; Muñoz-Murillo, A.; Oord, R.; van Bergen-Brenkman, T.; Wels, B.; Bruijninx, P. C. a.; Weckhuysen, B. M. Skeletal Isomerisation of Oleic Acid over Ferrierite: Influence of Acid Site Number, Accessibility and Strength on Activity and Selectivity. *J. Catal.* **2015**, *329*, 195–205. <https://doi.org/10.1016/j.jcat.2015.05.013>.
- (71) Claude, M. C.; Vanbutsele, G.; Martens, J. A. Dimethyl Branching of Long N-Alkanes in the Range from Decane to Tetracosane on Pt / H – ZSM-22 Bifunctional Catalyst. **2001**, *231*, 213–231. <https://doi.org/10.1006/jcat.2001.3325>.
- (72) Lee, S. H.; Shin, C. H.; Hong, S. B. Investigations into the Origin of the Remarkable Catalytic Performance of Aged H-Ferrierite for the Skeletal Isomerization of 1-Butene to Isobutene. *J. Catal.* **2004**, *223* (1), 200–211. <https://doi.org/10.1016/j.jcat.2004.01.029>.
- (73) Verboekend, D.; Caicedo-Realpe, R.; Bonilla, A.; Santiago, M.; Pérez-Ramírez, J. Properties and Functions of Hierarchical Ferrierite Zeolites Obtained by Sequential Post-Synthesis Treatments. *Chem. Mater.* **2010**, *22* (16), 4679–4689. <https://doi.org/10.1021/cm100886y>.
- (74) Zhang, S.; Zhang, Z. Fatty Acid Isomerization with Mesoporous Zeolites. WO 03/082464 A1, 2003.
- (75) Bolshakov, A.; de Poll, R. van; Bergen-Brenkman, T. van; Wiedemann, S. C. C.; Kosinov, N.; Hensen, E. J. M. Hierarchically Porous FER Zeolite Obtained via FAU Transformation for Fatty Acid Isomerization. *Appl. Catal. B Environ.* **2020**, *263*, 118356. <https://doi.org/10.1016/j.apcatb.2019.118356>.

## SYNOPSIS

This perspective discusses the current state-of-the-art and shortcomings regarding the high selective valorization of fatty acids to branched fatty acids, a high-end oleochemical product, using zeolites.

FOR TABLE OF CONTENTS USE ONLY



## BIOGRAPHIES

### Dorien Kerstens



Dorien Kerstens (1992) obtained her MSc degree in Bioscience Engineering (Catalytic Technology) at KU Leuven (Belgium) in 2015. She did her master's thesis at the Centre for

Surface Chemistry and Catalysis under the guidance of prof Bert F. Sels, where she explored the use of zeolites for the valorization of oils and fats. She is currently doing a PhD in the same research group on the role of zeolites in the oleochemistry.

### **Sofie Van Praet**



Sofie Van Praet obtained her MSc degree in Bioscience Engineering (Catalytic Technology) at KU Leuven in 2019. She completed her master thesis at the Centre for Surface Chemistry and Catalysis under the guidance of Prof. Bert F. Sels, where she developed an in-depth analysis procedure for branched fatty acids. She is currently carrying out PhD research in the same group, focusing on the reductive amination of carbohydrates using heterogeneous catalysts.

### **Luca Verhoeven**



Luca Verhoeven (1994) obtained his MSc degree in Chemistry at UGent in 2017. He performed his joint thesis at the Centre for Ordered Materials, Organometallics and Catalysis (COMOC) under guidance of Prof. Pascal Van Der Voort and the Polymer Chemistry and Biomaterials Group (PBM) under guidance of Prof. Peter Dubruel. In this thesis, he developed a method for the deposition of Pt@MOF particles in a matrix of electrospun polycaprolactone nanofibers which functioned as a catalytic carpet for hydrogenation reactions. He is currently working at Oleon nv as an R&D engineer for the BASE oleochemicals division.

**Pieter Struelens**



Pieter Struelens (1979) holds a MSc degree in chemistry obtained at VUB university (Belgium). A dissertation handling dioxins and PCB analysis on animal fats was made. Thereafter, a doctoral thesis, promoted by Prof. Em. Pierre Jacobs, dealing with methanol transformation on acid catalysts was successfully submitted at the Centre for Surface Chemistry and Catalysis KU Leuven, Belgium. Currently, he is employed as an R&D Manager leading the R&D activities for lubricant, oilfield and industrial chemicals for Oleon nv, Belgium.

### **Bert Sels**



Bert F. Sels (1972), currently full professor at KU Leuven, obtained his PhD in 2000 in the field of heterogeneous oxidation catalysis. He was director of the Centre for Surface Chemistry and Catalysis (COK, 2015-2018), and started in 2019 at KU Leuven a new division called 'Centre for Sustainable Catalysis and Engineering, CSCE'. His research activities encompass the design of heterogeneous catalysts for the future challenges in industrial organic and environmental catalysis. His expertise includes heterogeneous catalysis in biorefineries and biofactories, design of hierarchically structured materials such as zeolites and carbons for catalysis, and identification of catalytically active sites for small molecule activation using spectroscopy and kinetics.