3
Isostearic Acid: A Unique Fatty Acid with Great Potential

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3.1
Introduction

The total world production of the major oils and fats in 2014 is estimated at around 207 million metric tons [1, 2], of which palm, soybean, and rapeseed together account for two-thirds (Figure 3.1). Animal fats (tallow, lard, butter, and fish) contribute around approximately 12.5% of the total, and specialty vegetable oils, such as corn, linseed, and castor oil, constitute 2.6%. The annual growth rate in production of the major vegetable oils, over the period 2010 – 2014 is around 4.2%.

In 2011, it was estimated that about 70 – 75% of the global production of oils and fats was consumed in human nutrition, with the remainder going into animal feed, biofuels, and oleochemicals [3]. In recent years, fuel uses, biodiesel production in particular, and cogeneration in power stations have increased the nonfood demand for vegetable oils. Their large-scale use for fuel and energy is however generally uneconomic in the absence of financial incentives. The ongoing debate on the use of food-grade vegetable oils in both industrial applications and for fuel production has an impact on the assessment of the net environmental and sustainability benefits of (bio-based) raw material choices in these sectors. The focal point of these discussions has been biodiesel and power generation since, compared to chemical and industrial uses, these have the potential to consume vast amounts of natural resources. A dramatic illustration of the potential problems was seen in 2006 – 2007, when riots in Mexico over a growing shortage of the food staple corn tortillas, were blamed on the rapidly rising demand for corn ethanol created by the United States biofuel industry [4].

Recognition that food-grade vegetable oils alone cannot economically or practically meet a significant part of the demand for vehicle fuels has led to research into second- and third-generation biofuels based on abundant alternative feedstocks, such as lignocellulosic biomass, and municipal and agricultural waste streams. Biodiesel producers have also adapted their processes to handle tallow, used cooking oil, yellow greases, and other lipid streams not suitable for
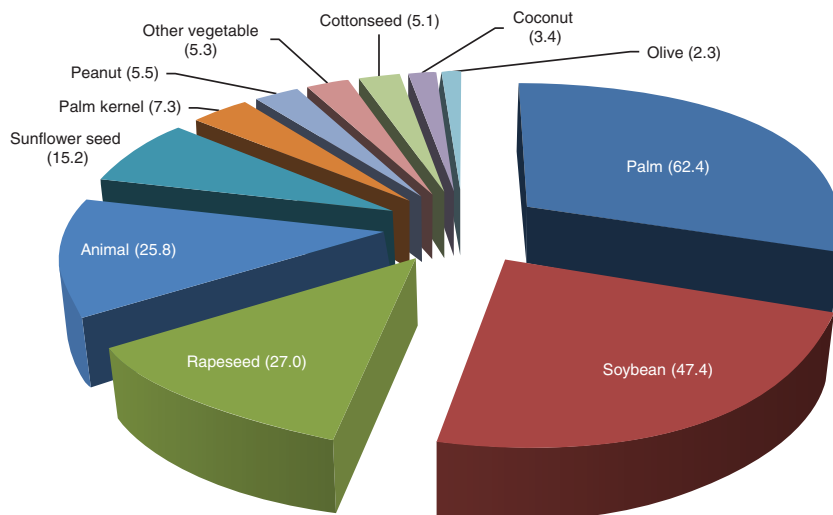
Figure 3.1 World production of major vegetable oils and fats in 2014 (in million metric tons) [1, 2].

human consumption. Alternative lipid sources, such as algae, are also under intense investigation [5], both for fuel and chemicals production.

3.2
Biorefinery and Related Concepts

The use of natural and agricultural feedstocks for the production of chemicals has grown rapidly in recent years and has led to the development of integrated "biorefinery" concepts [6] as a way to achieve the scale and economics to compete with current mineral and petrochemical routes. A parallel strategy has been followed to adapt existing mineral oil refinery infrastructure, so that the bio-based feedstocks can be used directly, or with limited modification, in the downstream refinery operations. The development of supporting technologies, and the relative prices of mineral sources and agricultural commodities, will determine the rate at which this transformation occurs. A perspective on opportunities for bio-based chemical production in the Port of Rotterdam, for instance, estimated that 10−15% of the fossil oil-based bulk chemicals could be substituted by bio-based equivalents within 10 years [7].

Sugars, starches, and other carbohydrates can be converted to small molecules with high functionality, making them good starting points for production of bio-based monomers and chemicals. Some commercial examples of bio-based chemical production include (poly)ethylene from sugarcane ethanol (Braskem [8]), (poly)lactic acid from corn sugar (NatureWorks [9]), 1,3-propanediol from fermentation of corn syrup (DuPont [10]), succinic acid from fermentation of various sugars (Bioamber [11]), and methanol from glycerol and biogas

(BioMCN [12]). Economically feasible alternative feedstocks are available for glycols, isopropanol, acetone, and methyl ethyl ketone, and production processes already exist or are in advanced stages of development [7].

By contrast, oils and fats have long carbon chains and limited functionality, making them more suited to production of hydrocarbon-rich chemicals and products. The already well-established oleochemical industry deals with such conversions and can be considered as biorefineries, in which crude vegetable oils and animal fats are used as raw materials for a diverse range of chemicals [13]; indeed, the origins of the industry can be traced back to the French scientist Michel Eugene Chevreul (1786–1889), following the publication of his pioneering research "Recherches Chimiques sur les Corps Gras d'Origine Animale" in 1823 [14]. The sector has continued to develop, however, and current lipid research in Europe focuses mainly on functionalization of vegetable oils and their derivatives, especially of the double bond, for the production of specialty chemicals and monomers. Enzymatic and fermentation processes are also developing alongside more traditional chemical routes [15–22]. Furthermore, developments in crop breeding technology have a growing importance in industrial oleochemistry, opening up the possibility for new and improved oilseed varieties with more tailored compositions in an economically viable way [23]; previously, oleochemical feedstocks were intrinsically linked to food production and were rarely developed solely for the production of chemicals and industrial products.

The renaissance in oleochemistry is not confined to academia, and important industrial developments have been seen in the last decade: in the United States, Elevance Renewable Sciences [24] has pioneered the use of metathesis to produce a range of specialty chemicals, ingredients, and feedstocks based on vegetable oils, many of which are novel. In Europe, Novamont [25] is combining both oleochemistry and carbohydrate chemistry in the development of biodegradable polymers for packaging materials, within a broad and highly integrated biorefinery concept; in this example, the unsaturated vegetable oils are subjected to a catalyzed oxidative cleavage reaction in the presence of hydrogen peroxide, forming mono- and difunctional acids, which can be considered basic (lipid-derived) platform chemicals.

In summary, the future of oleochemistry looks bright; in addition to the growth of the traditional oleochemical products, driven in part by improving economics compared to mineral oil-based chemicals, developments in raw materials, process technologies, and in the combination with other plant-based materials, promise to further expand the utilization of oils and fats in industrial products.

3.3
Sustainability of Oils and Fats for Industrial Applications

In 2005, production of palm oil overtook soybean oil to gain pole position as the major vegetable oil source. In 2014, palm accounted for 62 million metric tons versus 47 million tons for soybean oil. The rapid rise of palm oil production can be

attributed to both economic and agronomic factors; palm oil yields (including the palm kernel oil) are around 5 metric tons $ha^{-1} yr^{-1}$ (predicted to rise in the short term to more than 6 metric tons $ha^{-1} yr^{-1}$), compared to 0.7 for rapeseed and 0.4 for soybean [26]. In this comparison, it is important to add that soybeans contain only 20% of oil and are grown primarily for their protein-rich meal. Palm oil is therefore the most efficient of the major vegetable oil crops in terms of land use.

This rapid growth has come with an environmental price tag; unchecked deforestation, destruction of natural habitats (e.g., of the orang-utan), and air pollution from burning of rain forests are major issues connected to the palm oil industry. However, due to the work of the certification body Roundtable on Sustainable Palm Oil [27] (RSPO) and the intervention of activist groups such as Greenpeace, there is a strong momentum in the European oil and fat industry toward the development of sustainable palm oil supply chains. Major multinational food producers, such as Unilever, Nestlé, and Procter & Gamble (P&G), are committed to sourcing palm oil from sustainable production sites, allowing the oil to be traced back to the individual mills. With this development and well-publicized commitments from the multinationals, the primacy of palm in the oils and fats industry looks assured for years to come.

Several Malaysian and Indonesian palm producers have purchased European oleochemical companies in recent years, and others have set up distribution networks to supply the European market. As a result, imported palm streams have, to a large extent, displaced animal fats as the key oleochemical raw material. These vertically integrated producers are now moving further down the supply chain into production of fatty alcohols, specialty chemicals, and surfactants [28]. This has parallels with the growth of the petrochemical industry during the postwar years, in which oil producers moved downstream to convert the crude oil fractions into value-added chemicals and products, mitigating the volatility in oil price and helping to stabilize profits.

Producers of other major oil crops are developing their own criteria for sustainability relevant for the conditions and geographies where they are grown: schemes such as the German REDCert certification scheme [29] and International Sustainability and Carbon Certification (ISCC) [30] have been set up to support the development and monitoring of sustainable supply chains. Imported crude vegetable oils, such as soybean and canola, have additional supply chain complexities to meet the consumer demand in Europe for traceable non-genetically-modified (GM) oils. Although current European Union (EU) rules allow GM crops to be grown anywhere within the EU after approval by the European Food Safety Authority (EFSA) and the oils of GM crops can be imported for industrial and food use, consumer-related markets may demand a non-GM option.

Both fuel and industrial producers target by-products from vegetable oil refining as raw materials: acid oils, fatty acid distillates, and similar. However, these streams have a limited availability. They are typically about 5% of the total vegetable oil refinery output, and there are established applications in oleochemicals, animal feed, and others with which any new use must compete. The reality for vegetable oil refining is that very little of the output is a genuine "waste stream,"

when that is defined as a stream with zero or negative value – indeed some by-products have a higher value than the incoming crude oil, and thus positively contribute to the economics of the refinery. By-products are generally indexed in value to the crude vegetable oil, which they may substitute when the difference in price is sufficient to overcome the extra costs to purify or process them further. Tall oil provides an interesting example of such a lipid by-product and is obtained from the Kraft or sulfate process for paper pulp production from pinewood. It is used exclusively for industrial purposes and consists of a complex mixture of about 50% fatty acids, 40% rosin acids, and 10% unsaponifiable fraction, which are separately purified and sold for use in a wide range of applications [31].

The use of oils and fats for industrial applications has thus been growing steadily over recent years, at a faster rate than for human nutrition. Furthermore, vegetable oils experience a growing share of the industrial and chemical sector as a sustainable source of hydrocarbon-rich feedstock, through substitution of traditionally mineral oil-based chemicals and products as a sustainable source of hydrocarbon-rich feedstock.

The development of green chemistry and biorefinery concepts also gives a new momentum to the field of oleochemistry. In this chapter, we give a short introduction to the modern oleochemical industry and illustrate the renewed interest in oil and fat chemistry with recent research in the catalytic isomerization of linear fatty acids to branched acids – "isostearic acid (ISAC)." The history of ISAC production and current routes to branched fatty acids (natural and fossil derived) are discussed. The special properties of ISAC are illustrated through its use in applications and processes inaccessible to conventional fatty acids. Finally, the latest developments in zeolite catalysis for its selective manufacture are presented.

3.4
Fatty Acids

Whereas food and food production uses predominantly refined oils and fats, fatty acids are the major raw materials for the production of chemicals and industrial products (excluding direct fuel and biodiesel uses). World consumption and production of fatty acids in 2011 were estimated at 6.0 million tons (excluding production of fatty alcohols), expected to rise to 7.0 million tons by 2016. Western Europe consumes 1.5 million tons (including 170 000 t of tall oil fatty acids (TOFAs)) but produces only 0.9 million tons, the balance being mainly palm-based import streams from Southeast Asia [32]. Soaps, chemicals, surfactants, lubricants, and coatings are some of the important applications of fatty acids; in general, their growth follows Gross Domestic Product (GDP) growth in the region of consumption, reflecting the broad range of end-use industries.

Several processes are described for the hydrolysis ("splitting") of fats and oils into fatty acids and glycerol [33], including enzymatic splitting using lipases, but the dominant commercial process is high-pressure continuous splitting, known as the *Colgate–Emery process*; water is contacted in countercurrent flow with the oil or fat at around 250 °C and 50 bar pressure, in a mass ratio of approximately

2 : 1 fat/water, for residence times of 1−3 h. The resulting hydrolysis of the oil or fat to fatty acids and glycerol is almost complete, with yields of up to 99% of the theoretical value. The dilute glycerol stream (10−15 wt%) can be purified and concentrated to 85−99 wt% by evaporation and distillation and is used in many industrial, consumer, and food products.

The crude fatty acids can then be subjected to a variety of downstream physical processes, such as:

- *Distillation.* The crude fatty acids are purified by distillation to remove odor, color, impurities, and volatile components.
- *Crystallization.* Saturated acids can be separated from unsaturated acids by crystallization, using processes based on solvents, water/surfactants, or simply cooling the fatty acids and pressing out the liquid fraction ("dry fractionation"). Commercial-grade oleic acid is made by all of these methods, starting from fatty acids derived from tallow fat or palm oil.
- *Fractionation.* The term "fractionation" in the oleochemical industry refers to a distillation process in which fatty acids are separated based on the boiling point of the different chain lengths. For example, coconut fatty acids, which consist of carbon chains from C_8 to C_{18}, are fractionated into a $C_8 - C_{10}$ fatty acid cut, which has a high value as a raw material for lubricants, cosmetics, and food supplements, and a $C_{12} - C_{18}$ fatty acid cut, which is suitable for soaps and detergents, for example.

In addition to physical processes, chemical modifications, such as hydrogenation, esterification, amidation, ethoxylation, and polymerization, are all currently performed on industrial scale (Figure 3.2).
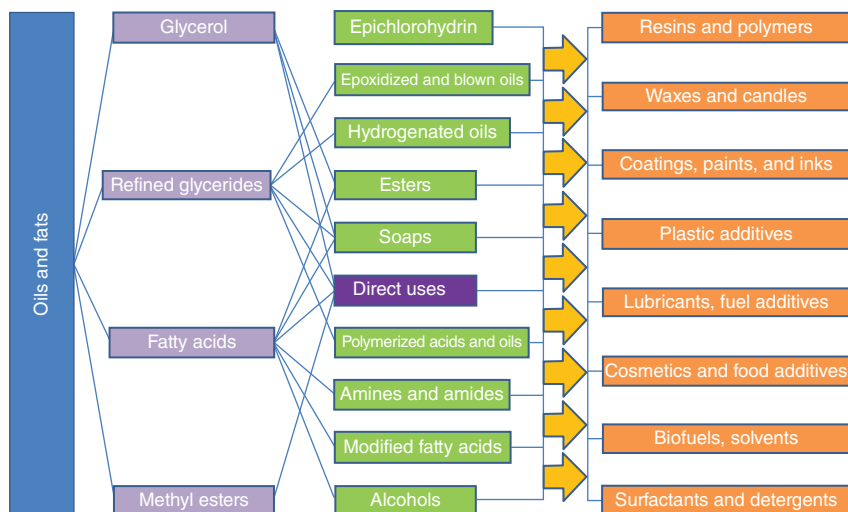
Figure 3.2 Schematic overview of the different conversion routes of oils and fats and the applications of the oleochemicals derived from them. The "modified fatty acids" group includes conjugated, branched, hydroxylated, and hydrogenated fatty acids.

3.5
Polymerization of Fatty Acids

3.5.1
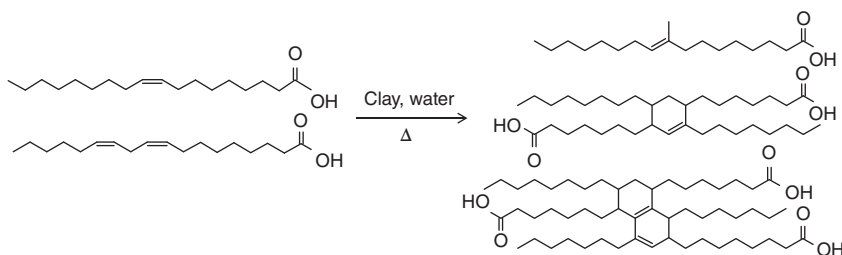**Thermal Polymerization**

Thermal polymerization of vegetable oils to produce bodied (thickened) oils was practiced from the beginning of the twentieth century, but in the 1940s attention turned to polymerization of unsaturated fatty acids and their monoesters for use in the manufacture of polymers [34]. The investigations of Bradley and Johnston ([35] and subsequent publications) showed that the main products from thermal polymerization of fatty methyl esters were dimeric and that the structures formed were determined mainly by the degree of unsaturation of the starting material. Johnston hydrogenated the resulting oligomers to polyhydric fatty alcohols using a copper chromite catalyst [36].

The uncatalyzed thermal polymerization of unsaturated fatty acids was performed industrially by Emery Industries in the United States in 1948. TOFA, a by-product of paper production, was the preferred feedstock, being highly unsaturated and therefore sufficiently reactive. The dimer acids were used in the production of polyamide resins for inks and adhesives. However, a process for polymerization of unsaturated fatty acids, and their purification and use in making synthetic resins with improved properties, was described as early as 1935 [37].

3.5.2
Clay-Catalyzed Polymerization

A step change in fatty acid polymerization was achieved in 1957 when Barrett, Goebel, and Myers developed a clay-catalyzed process based on swelling montmorillonite-rich smectite clays (Scheme 3.1) [38, 39].

Scheme 3.1 Clay-catalyzed polymerization of commercial oleic acid, which contains mainly linoleic acid in addition to oleic acid. The reaction product is a complex mixture of branched (monomeric) oleic acid, C_{36} dimeric acids, and C_{54} trimeric acids (typical structures are shown for each fraction; note that all fractions contain many isomers).

There are several key advantages of this process over thermal polymerization, namely:

- Reaction times are shorter, and polymerization temperatures lower.
- A wider range of feedstocks can be used; the clay-catalyzed process can polymerize both polyunsaturated and predominantly monounsaturated fatty acids, such as tallow oleic acid.
- Better control is achieved over the ratio of dimeric to trimeric and higher fatty acids, with less dependence on the feedstock composition, due to the constrained reaction sites within the clay interlayers.
- Reaction products with lighter colors are achieved.

A further advantage of the catalyzed process over the thermal one was the quality of the "monomer acids," that is, the non-polymerized fraction of the feed. In the thermal process, it consisted mainly of inert and unreacted fatty acids. However, a different monomer composition was observed in the clay-catalyzed process; the monomeric fraction was not characterized in detail until the 1970s, when McMahon identified it to be rich in methyl-branched saturated and unsaturated acids [40]. Haase, in the late 1980s, further characterized the hydrogenated branched fraction, dividing it into mono- and multiple methyl-branched fatty acids [41]. These methyl-branched isomers, once purified and hydrogenated, became the commercial product now better known as *isostearic acid*.

In later improvements to the clay-catalyzed process, certain alkali and alkaline-earth metal salts were shown to modify the clay interlayer distances and therefore provide a means to fine-tune the process toward higher polymerized fatty acid yields [42]. The modern process includes downstream modifications to the polymerized acids, such as hydrogenation, and further purification of the polymerized acids into dimeric (>98%) and trimeric (>80%) fractions. Derivatives, such as the diol and the diamine, are also commercially available.

3.6
ISAC

During the first decades of the clay-catalyzed process, monomer acids were distilled off from the more valuable polymerized fatty acids and sold as cost-effective fatty acids for a range of applications. Later, the branched acids were purified by solvent separation from the saturated and straight-chain acids and hydrogenated to form what became known as *isostearic acid*, commonly abbreviated as ISAC (Figure 3.3). The first commercial ISAC was produced by Emery Industries, most likely based on the patented process described by Peters in 1957 [43].

It took time for the unique properties of ISAC to be fully appreciated, and markets and applications had to be developed; the relatively high production costs meant that performance benefits had to be demonstrated versus cheaper liquid fatty acids such as tallow oleic acid, rapeseed, and TOFAs (themselves feedstocks for the isomerization/polymerization process). Furthermore, the process could be
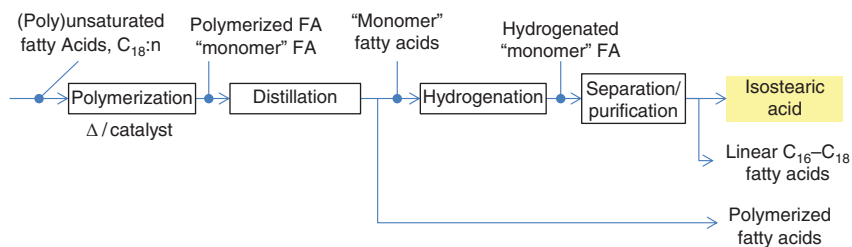
Figure 3.3 Current process for production of isostearic acid and polymerized fatty acids.

steered toward ISAC only to a limited extent, effectively linking ISAC production to polymerized fatty acid demand.

Despite these practical hurdles, the use of ISAC has grown steadily to the point where it can no longer be considered as a "coproduct," but as a high-value functional oleochemical in its own right. The properties of ISAC are unique within the class of vegetable-derived fatty acids, allowing it to be used in applications where the technical performance of commodity fatty acids is insufficient, thus expanding the use of renewable resources in industrial and consumer applications.

3.7
Other Branched Chain Fatty Acids

3.7.1
Natural

C_{20} chain fatty acids with monomethyl branching at the iso- (ω-1) and anteiso- (ω-2) positions are the major constituents of fatty acids bonded to the surface of human hair and mammalian fur [44]. Similar branched structures are found in the milk fat of cows (and other mammals), constituting about 2% of the total fatty acids [45]. Iso- and anteiso-fatty acids with carbon chain lengths of $C_4 - C_{15}$, in the form of wax esters, are major components of lanolin (purified sheep wool grease). Lanolin is a complex mix of lipid components, comprising esters and alcohols as the major fractions [46].

Branched chain fatty acids with methyl groups present on all positions along the alkyl chain have furthermore been isolated from bacteria, although only in minor amounts [47]. Dembitsky presented a comprehensive survey of naturally occurring neoacids (in this definition, "neo" refers to an alkyl chain terminating with a *tert*-butyl group, which differs from the definition for synthetic branched acids covered in Section 3.7.2). The sources identified include plants, fungi, algae, marine invertebrates, and microorganisms [48].

Although interesting, and in many cases serving important biological functions, most of these sources of natural branched lipids are not sufficiently abundant, accessible, or concentrated to provide a viable feedstock source for industrial-scale production. Lanolin is a notable exception; it is purified, separated into different

fractions and further functionalized, and represents an important specialty lipid with applications in cosmetics, pharmaceuticals, and industrial products.

3.7.2
Petrochemical

Most of the branched alcohols, acids, and other branched derivatives are currently provided by the petrochemical industry, using ethylene, propylene, paraffins, and (linear and branched) olefins as hydrocarbon sources. Coal and natural gas, current feedstocks for Fischer–Tropsch synthesis processes, can also be considered as raw materials.

Branched acids from petrochemical sources generally have shorter carbon chains and more and/or longer chain branching compared to ISAC. The main commercial route to synthetic branched acids is by carboxylation of olefins, using a modified oxo (carbonylation) process (Scheme 3.2). The olefins themselves are derived from a variety of petrochemical routes and can be branched or linear, internal, or terminal (α olefins). Alternatively, though less common, oxo alcohols can be oxidized under basic conditions to the corresponding acids.
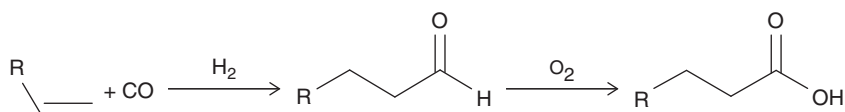
Scheme 3.2 Production of "oxo" acids using hydroformylation and oxidation; R is a branched or linear alkyl chain.

ExxonMobil's "neoacids" are produced commercially by a modified oxo process (Koch–Haaf) and are highly branched [49]. In the presence of a strong acid catalyst, the protonated olefins can rearrange to the more stable tertiary carbocation, which after carbonylation and addition of water yields a tertiary carboxylic acid group (Scheme 3.3). This "neo" structure results in high steric hindrance, which in turn imparts excellent thermal and hydrolytic stability to derivatives. Momentive Specialty Chemicals produce the Versatic™ Acid 10 (neodecanoic acid) by a similar route. The most important oxo-derived acids have total carbon C_9–C_{11} chains and are used as intermediates in the production of, for example, PVC stabilizers, organic peroxide initiators, and metal salt-based catalysts.
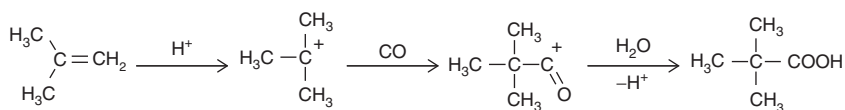
Scheme 3.3 Production of neopentanoic acid from isobutene via the two-stage Koch reaction.

Closer in structure to ISAC are the C_{16}–C_{18} "isostearic" acids of Nissan Chemical (Fineoxocol® trade name), also derived from an oxo process via

oxidation of the corresponding alcohol – a highly branched and a less branched alternative are offered. Due to the absence of linear fatty acids and relatively highly branched structures, the pour points of these synthetic acids are very low (below −30 °C). The published applications of the Fineoxocol® acids are similar to those of ISAC.

Paraffin waxes (linear and branched) can be oxidized with air directly to fatty acids at about 110−130 °C in the presence of cobalt or manganese salts. This route was particularly prevalent in Russia and former Eastern Europe, where an ample supply of wax was available from the petroleum refineries. However, it involves a free radical oxidation process which produces a complex mixture of products including linear and branched acids, esters, aldehydes, and ketones, and isolation of the branched fatty acids requires an expensive work-up process [50]. Production of fatty acids by this route is now of relatively minor importance.

Some specific branched chain alcohols use similar synthetic routes to the acids and can be considered alternatives to isostearyl alcohol, the hydrogenated derivative of ISAC. Isostearyl alcohol is an important personal care ingredient. Shell's Neodol® 67 process, developed in collaboration with P&G for the detergent market, produces lightly branched $C_{16}-C_{17}$ fatty alcohols, structurally close to isostearyl alcohol (Figure 3.4). Notably, the process uses a medium-pore zeolite with unidimensional channels of approximately 0.4−0.7 nm (hydrogen-form ferrierites being preferred) to isomerize linear internal olefins to predominantly (mono-) methyl-branched olefins [51], which are then selectively hydroformylated to the primary alcohol (Figure 3.4). The alcohols, when ethoxylated and/or sulfated, form detergent actives with excellent properties; advantages cited include excellent cold water solubility (despite the longer alkyl chain length compared to conventional detergent surfactants), good tolerance to calcium salts ("hard water"), acceptable biodegradability, and superior surface activity [52].

It is anticipated that the possible growth in Fischer−Tropsch synthesis processes will yield alternative sources of lightly branched olefins from wax cracking as potential raw material sources for the Neodol® 67-type products.

Guerbet alcohols are produced from linear alcohols at high temperature and in the presence of a base and a hydrogen transfer catalyst (copper or Raney nickel). The four-step synthesis route involves oxidation to the aldehyde, aldol condensation, dehydration, and finally hydrogenation to form the branched alcohol (Scheme 3.4). The branching is exclusively on the beta position and of
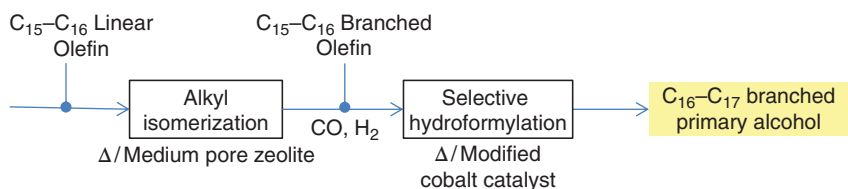
Figure 3.4 Production of $C_{16}-C_{17}$ branched primary alcohols (Neodol® 67) from C_{15} to C_{16} linear olefins.
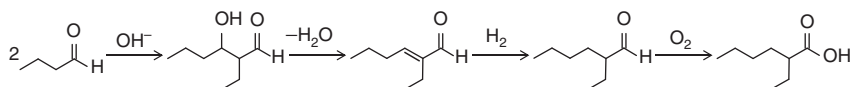
Scheme 3.4 Production of 2-ethylhexanoic acid via the aldol condensation of butanal.

chain length smaller by two carbons than the parent alcohol. This structure gives a significant depression in melting point, making them useful fatty materials for cosmetics and homecare products, a.o. [53]. The corresponding acids can be formed by oxidation of the aldehyde; one of the most important commercial synthetic acids, 2-ethylhexanoic acid, is produced in this way starting from 1-butanal.

Biermann *et al*. have reviewed a range of (mainly) preparative synthesis routes to branched acids, starting from natural (linear) unsaturated fatty acids and methyl esters [54]. Radical additions, Friedel–Crafts alkylations, transition metal-catalyzed additions, and zeolite-induced skeletal isomerization are covered in detail.

3.8
Properties of ISAC

Kinsman has collated and reviewed the physical properties of ISAC and other branched chain acids [55]. This work is further expanded in a book chapter dedicated to branched fatty acids in [56]. More recently, Ngo has measured a number of important physical properties of ISAC (and some of its esters), produced by a zeolite-catalyzed route [57].

In most cases, ISAC exhibits properties which combine the "best" features of oleic acid (*cis*-9-octadecenoic acid, OA) and stearic acid (octadecanoic acid). Some of the key attributes for industrial and consumer applications are discussed later in the following sections.

3.8.1
Thermal and Oxidative Stability

ISAC is comparable in thermal and oxidative stability to stearic acid: this makes it well suited to applications where long shelf life and/or elevated usage temperatures are required. Data from the Kinsman work [55] is illustrative; in an oxygen absorption test performed at $60\,°C$, ISAC was stable up to 100 days, while commercial-grade oleic acid only reached $1-7$ days and technical-grade stearic acid (with a residual unsaturation given by the iodine value of $5\,g\,I_2/100\,g$) 25 days. Similarly, Ngo compared the oxidative stability of the methyl ester of purified ISAC with soybean oil methyl esters at $110\,°C$; the ISAC fatty acid methyl esters were 18 times more stable relative to the soybean fatty acid methyl esters according to test [57].

3.8.2
Low-Temperature Liquidity

Liquidity at low temperature is a required property for fatty acid-based ingredients used in outdoor and refrigerated environments, especially in markets such as lubricants. More generally, a liquid fatty acid is easier to store, transport, process, and formulate.

When purified to remove most of the linear saturated fatty acids, ISAC has good cold flow properties, comparable to oleic acid; this is carried over into derivatives such as esters. The branching pattern of oleic acid isomerized using a zeolite shows a skewed distribution around the midpoint [58]. This midpoint methyl branching gives the maximum melting point depression, as confirmed by the study of Cason on C_{19} chain monomethyl-branched fatty acids in which the branching position was systematically varied [59]; it is, however, the complex isomeric mix which accounts for the liquidity in commercial ISAC, since the study of Cason indicates that the pure isomers are all solid at room temperature.

An additional feature in commercial ISAC is the presence of multiple (methyl-) branched species, which when purified by solvent crystallization reach melting points as low as $-54\,°C$ [41]; by comparison, a eutectic mixture of (unsaturated) oleic and linoleic fatty acids has a melting point of about $-10\,°C$ [60].

3.8.3
Solubility

Derivatives of ISAC show improved solubility across a range of solvent types and polarities compared to the analogous stearic acid derivatives, which makes them easier to formulate and apply in industrial and consumer products. For example, the isostearate salts of zinc and lead were tested in twelve solvents of broadly different polarities and were shown to be compatible with more solvents than either the oleate or stearate analogs [61]. In aqueous solution, the sodium soap of ISAC has a solubility of approximately 15 wt% in water at room temperature, comparable to sodium oleate, whereas sodium stearate is only soluble to approximately 1 wt% [61].

3.8.4
Biodegradability

In general, the inclusion of an alkyl branch in the hydrocarbon chain of a fatty molecule hinders its biodegradability; hence it is important to establish the impact when ISAC and its derivatives are to be developed for use in environmentally sensitive applications.

Commercial ISAC has been tested for biodegradability according to OECD Guideline 301 B (Ready Biodegradability: CO_2 Evolution Test), and the results published on the website of the European Chemicals Agency [62] in support of

REACH registration. ISAC is confirmed to be "readily biodegradable" in this test, meeting the criteria of at least 60% conversion to CO_2 in a 28-day period.

Ngo has studied the biodegradation of ISAC produced by the ferrierite-catalyzed isomerization of high-purity oleic acid [63]. Three strains of *Pseudomonas* bacteria were selected, and all were able to metabolize the ISAC to a good extent, while new linear and/or branched chain fatty acids were formed as products of partial degradation. The results are not directly comparable to the OECD 301 B test, but confirm that ISAC can be readily utilized by bacteria as a carbon source and is thus suitable for use in environmentally sensitive applications where losses and spills could occur.

For a more comprehensive review of the physical properties of natural and synthetic branched acids, the reader is directed to the review of Kinsman [55].

3.9
Applications of ISAC

Due to the (currently) relatively high costs of production and purification, ISAC is used in more demanding applications where the properties listed earlier in section 3.8 are particularly valued. Lubricants, cosmetics/personal care ingredients, and a wide range of industrial applications are important markets for ISAC, and these are discussed in more detail in the following sections (Table 3.1).

3.9.1
Lubricants

Currently, biolubricants constitute only a minor part of the total lubricant market, estimated as approximately 3% in the EU in 2012 [64], although with a moderately

Table 3.1 Overview of the major markets and applications of ISAC and its derivatives, based on patent and published literature.

Markets	Applications	Key properties	References
Lubricant	Metalworking, gear oils, 2-/4-stroke engines, friction modifiers	Oxidative and thermal stability, low toxicity, biodegradability, dispersing lubricity and liquidity	[66–74]
Cosmetic and personal care	Skin and hair care, color cosmetic, sun cream, toiletries	Liquidity, odor and color stability, skin feel, substantivity, water resistance, dispersing and emulsifying	[75–82]
Industrials	Textile softening	Rewettability	[83]
	Metal paste	Dispersing	[84]
	Paper sizing	Water resistance, lubricity	[89]

positive legislative climate this share is expected to double by 2020. Wagner has stated that vegetable-derived lubricants have the technical potential to substitute over 90% of the mineral oil-based lubricants currently in use [65]. However, the considerable cost gap between mineral and vegetable oils must reduce further to encourage switching, and some inherent functional weaknesses need to be overcome. ISAC has great potential here, addressing key concerns regarding oxidative/thermal stability and low-temperature properties, which are commonly cited as stumbling blocks to further development of vegetable-based lubricants. Esters of ISAC are used as components of base oils for the production of synthetic lubricants and greases. In addition to their inherent low toxicity and good biodegradability [66], they exhibit high flashpoints, low pour points, and good application properties. Important base oils include polyol ISAC esters based on pentaerythritol [67], trimethylolpropane (TMP) [68], and neopentyl glycol (NPG). In some cases, the purified ISAC can be substituted by the monomer acids when the application is tolerant of the slightly inferior low-temperature properties and stability.

Important applications within the broad classification of lubricants include metalworking fluids, industrial gear oils [69], two- and four-stroke automotive engines [70], hydraulic fluids [71], greases, and textile lubricants. ISAC-derived amines and amides are also used as friction modifiers in transmission fluids [72, 73]. For a recent survey of synthetic lubricant esters, see [74].

3.9.2
Cosmetics and Personal Care

ISAC and derivatives are important raw materials in the production of a.o. emollients and emulsifiers for cosmetic and skin care products. ISAC esters have similar physical properties to those of unsaturated fatty acids like oleic acid, but with the important benefit of superior odor and color stability (and sometimes additional desirable sensory properties). ISAC can form permeable lipid films on the skin, increasing moisture transport and supporting the penetration of other ingredients through the stratum corneum, making them useful carriers for active ingredients [75].

ISAC esters of light alcohols give a light emolliency, with no oiliness or stickiness. The capryl ester is reported to give similar sensory properties to cyclomethicones (cyclic polydimethylsiloxane polymers currently used in skin care and hair care products as a carrier and delivery system for active ingredients [76]). ISAC can be partially esterified to produce nonionic emulsifiers (e.g., polyglycerol, sorbitan, or polyethylene glycol esters). When fully esterified, they are emollient oils; depending on the structure and functionality of the alcohol/polyol used, a wide range of physical and sensory properties can be achieved, from light oils (e.g., isopropyl isostearate) to viscous, highly skin substantive, and water-repellent liquid waxes (e.g., pentaerythrityl tetraisostearate).

ISAC and derivatives are used to disperse metal oxides in sunscreen products [77, 78] and inorganic pigments in colour cosmetics [79]. High molecular weight isostearate esters based on, for example, oligomers of glycerol and pentaerythritol, are highly substantive, hydrolysis-resistant, and function to enhance gloss in, for example, lipsticks [80].

ISAC and derivatives are also used in hair conditioners, shampoos [81] and colorants, hand soaps, shaving products, deodorants, and nail polish removers. Thickening agents based on ISAC have also been reported (e.g., polyoxyalkylene ethers of glycerin or 1,2-propanediol, esterified with ISAC [82]).

3.9.3
Other Industrials

ISAC and derivatives are used in a very broad range of other markets and applications, including (production of) textiles, paper, plastic additives, surfactants, and detergents. Some examples are given in the following as an illustration of their scope of application.

Cationic surfactants, in particular quaternary nitrogen-containing ones, such as Evonik's Rewoquat® W 325 PG [bis-(isostearic acid amidoethyl)-*N*-polyethoxy-*N*-methylammonium methosulfate] are used in industrial textile softening [83]. The isostearic hydrophobe gives superior rewetting of certain fabrics; that is, it conditions and softens the fabric without excessively waterproofing it. This property has a clear analogy with the use of isostearic derivatives in topical skin care products, which permit the formation of protective yet water-permeable films.

ISAC provides a functional coating for metal and mineral particles used as fillers or pigments in polymer-based products such as plastics and paints; the carboxylic acid group binds to the particle surface, while the fatty chain allows solubilization in the polymer matrix, for example, alumina (surface modification of alumina hydrate with liquid fatty acids [84]). In the form of organo-titanate esters, this compatibilizing coating has broad application (inorganic – organic composites and methods of reacting the same with organotitanium compounds [85]), improving dispersion of the inorganic particles leading to lower melt viscosity, higher filler loadings, and improved physical/mechanical properties in polymer systems. ISAC also provides a dedusting coating for aluminum powder for use a.o. in aqueous slurry explosives [86].

In laundry detergents, formulations containing cationic ISAC derivatives impart antistatic properties to fabrics (ISAC, acrylamide cationic polymers [87], N-alkylisostearamides as antistatic agents [88]). Alkyl ketene dimers based on ISAC-rich fatty acids are used in the paper industry as sizing agents, with improved properties for ink-jet printing [89]. In PVC production, isostearate metal salts (such as zinc, calcium, and tin) are components of liquid stabilizer packages, while esters of ISAC can be used as plasticizers. Polyamide ink resins using ISAC as chain stoppers are claimed to show reduced blooming [90].

3.10
Selective Routes for the Production of ISAC

As shown earlier, ISAC has unique properties within the general class of fatty acids, due to its lightly branched structure. These properties are exploited in a variety of more demanding markets and applications, where commodity liquid vegetable fatty acids are unsuitable or inferior. Its current commercial production is linked to that of polymerized fatty acids (Scheme 3.1). This has several disadvantages, which hinder its further development, namely:

- ISAC coproduction with polymerized fatty acids requires a constant balancing of supply and demand; this limits in any case the supply growth rate to that of the polymer acids.
- Purification of ISAC requires multistep separation processes, which makes the end product costly to produce.
- The clay-catalyzed process offers limited scope to increase the yield of ISAC, and modifications to the process in this direction usually impact the quality of the polymerized acid fraction.
- Synthetic routes to branched fatty acids exist, but they are based on nonsustainable petrochemical sources and/or produce acids or alcohols with substantially different properties.

Therefore, there is a need for a more direct and cost-effective synthesis route to production of ISAC, which would decouple supply from polymerized fatty acid production and allow the unique properties to be fully exploited.

3.10.1
Optimization of the clay-catalyzed process

As mentioned in section 3.5.2, the current commercial clay-catalyzed process for production of ISAC uses a swelling clay in which, skeletal isomerization of the unsaturated fatty acids competes with oligomerization. For both products, the main reaction mechanism is believed to go via the same carbocation intermediate [91]. As a result, complete decoupling of these reactions cannot be achieved by optimization of the process conditions alone, and the catalyst system must be modified.

Oligomerization has been found to be favored by swelling of the clay using water and/or cations (e.g., Li^+), with an increase in oligomer yields from 35% to 55 wt% [92]. Although Brønsted acid sites (tetrahedral sites with Al^{3+} substitution of Si^{4+}) were confirmed as active sites, high yields require the simultaneous presence of octahedral sites (e.g., substitution of Si^{4+} by Mg^{2+}); binding of the carboxylic groups to the latter is believed to prevent poisoning of the tetrahedral sites [93]. Conversely, addition of a small amount of Brønsted acid (e.g., phosphoric acid) as cocatalyst significantly increases yields of the isomerized monomeric fatty acids (from 30% to 50 wt%) [92].

3.10.2
Zeolite-catalyzed branching in the petroleum industry

The replacement of the clay catalyst by a zeolite holds considerable promise for the decoupling of the two competing pathways. Their shape-selective properties are well known in the refining and petrochemical industry [94, 95] and have also been exploited for biomass conversion [96, 97]. The limited space of their intracrystalline volume inhibits the transition state formation from bimolecular reactions, suppressing di- and oligomeric fatty acids. Another advantage of zeolites for the OA skeletal isomerization is the ability to tailor their acidity, in terms of type (Brønsted/Lewis), density, and strength [98].

Shape selectivity effects have been widely studied for the skeletal isomerization of butene to isobutene catalyzed by zeolites and molecular sieves [95, 99–101]. This reaction was heavily studied up to the 1990s in order to meet the expected increasing demand in isobutene for the production of methyl *tert*-butyl ether. Since the US ban of this additive, the intermediate needs are restricted to the methacrylate, polyisobutene, and butyl rubber markets. High yields in isobutene require narrow-pore molecular sieves with 10-membered ring (MR) channels, such as MeAPO-11 [102], SAPO-11 [103, 104], Theta-1 [105], and Zeolite Socony-Mobil (ZSM)-22 (both TON, one-dimensional) [106], ZSM-23 (MTT, one-dimensional) [107], and ZSM-35 (FER) [108]. The three-dimensional 10-MR ZSM-5 (MFI) shows higher butene conversion but a much lower selectivity to isobutene; this is attributed to its larger void volume (from somewhat larger channels and their intersection) [107, 109, 110]. On the other hand, the 10-MR channels (3.1×7.5 Å) of heulandite (HEU) are believed to be too narrow for isobutene diffusion [100]. The best overall performance (activity, selectivity, and stability considerations) is achieved with ferrierite; this zeolite has a pore structure, made from the perpendicular crossing of one-dimensional 10-MR channels (4.2×5.4 Å) with one-dimensional 8-MR channels (3.4×4.7 Å); its moderately strong acidity is also thought to contribute to the low level of oligomerization and cracking reactions [99, 101]. Therefore, since its discovery by Shell, ferrierite has been widely adopted by industry for the isomerization of small olefins (e.g., ISOMPLUS® technology from Lyondell/CDtech) [111, 112] and is commercially available (e.g., from Tosoh Corporation and Zeolyst International).

The Pt/zeolite-based hydroisomerization of long-chain *n*-alkanes ($>C_7$) for the upgrade of petroleum fractions to high-grade fuels and lubricants is another reaction of relevance, known for its specific shape selectivity [95, 112]. It has been the research focus of a number of groups, leading to a detailed understanding of the molecular mechanism [113–115]. High selectivity to branching requires an "ideal" bifunctional catalyst with an optimized ratio between Pt sites for dehydrogenation/hydrogenation reactions and acid sites for the isomerization [114, 116]. The formation of multiple-branched alkanes, precursors of cracking, is again limited by the use of one-dimensional narrow molecular sieves with 10-MR channels, including SAPO-11, ZSM-22, and ZSM-23. Conversely,

significant cracking has been observed with zeolites with larger pores (beta and Ultra Stable Y (USY)) [117]. Besides the intermediate state selectivity, the use of the one-dimensional medium-pore zeolites also results in a specific methyl branching pattern that varies as a function of the *n*-alkane chain length. Product diffusion shape selectivity has been invoked to explain this observation [118–120]. Alternatively, the specific branching pattern has also been attributed to pore-mouth and key–lock catalysis, involving van der Waals interactions between the external surface and the long-chain alkanes [121–123]. Similar results, although less marked, have been described for the hydroisomerization of *n*-paraffins in the liquid phase [124]. Latest developments in zeolite engineering to enhance the external surface (and the number of pore mouths) while preserving its acidity have resulted in significant increase of the desired branched alkane yields: for example, hierarchical zeolites obtained by desilication in alkaline medium followed by acid washing [125], as well as by demetallation [126], have recently been reported.

3.10.3
Zeolite-catalyzed branching of fatty acids

The examples listed earlier suggest that zeolites could also represent a promising route to selective production of branched unsaturated fatty acids (BUFAs) in high yields, and have inspired several research groups to study the alkyl isomerization of OA. Focus has initially been on molecular sieves with large-sized channels, a choice motivated possibly because of the bulkiness of the BUFA compared to the isobutene and branched alkanes. Most of the information available is contained in patents, and BUFA yields are often difficult to compare due to the limited analytical information provided on product composition. For example, in some cases the chemical analysis data presented suggest significant purification. Table 3.2 summarizes the key developments.

The first example of zeolite catalysis for OA conversion to BUFA dates from 1997 [127]. The patent discloses the use of molecular sieves, such as protonated mordenite, with large-sized channels (12 MR, 6.5×7.0 Å) and linear pore structures. Reactions were carried out for 6 h at 280–300 °C with 4–8% catalyst loading. Addition of a small amount of water was shown to promote the conversion to BUFA, postulated to be due to the conversion of Lewis acid sites into Brønsted ones; this conclusion was drawn based on experiments using zeolite with Si/Al = 7.5 and Si/Al = 9.5. On the contrary, calcination of the catalyst for 2 h at 600 °C led to a significant decrease in BUFA yields, confirming the key role of Brønsted acidity. A direct comparison with the clay-catalyzed process demonstrated the superior selectivity of the protonated mordenite to monomeric acids, although the temperature used for the clay-catalyzed reaction was lower (240 °C) and the solidification point of the zeolite-derived product differed significantly from commercial isostearic. Zeolite USY (Si/Al = 3), and to a minor extent ZSM-5 (Si/Al = 7), gave lower BUFA yields under similar conditions, confirming the importance of the microstructure and/or its acidity.

Table 3.2 Literature overview for the selective OA alkyl isomerization in presence of zeolites and mesoporous materials.

Year	Type	Largest channels	Si/Al	Cat. (wt%)[a]	Reaction parameters	Catalytic testing	References
1997	Mordenite	12 MR (one-dimensional)	7.5 9.5	8	Water 280–300 °C 6 h	BUFA yields >60%; better than with clay, USY, and ZSM-5	[127]
1997	Mordenite, omega, L-type	12 MR (one-dimensional)	10	2.5	No water 265 °C 4 h	BUFA yields >50% with flat crystals	[128, 129]
2004	Beta, beta/Pd or Pt	12 MR (three-dimensional)	12.5	10	No water 250 °C 5 h	OA conversion up to 50%; range of feedstocks; large fraction of multiple branching	[132, 133]
2007	Beta	12 MR (three-dimensional)	13.5[b]	3	Water 250 °C 4 h	Conversion >65%	[134]
2004	MAS-5	Mesoporous	25	10	No water 250 °C 5 h	Conversion >60%; more efficient filtration; slower deactivation	[135, 136]
2007	Ferrierite	10 MR (two-dimensional)	8.5 27.5	2.5	Water 250 °C 6 h	Conversion >95%; BUFA yields >70%	[59, 137]
2012	Ferrierite/TPP	10 MR (two-dimensional)	8.5	5	Water 280 °C 6 h	Conversion >95%; BUFA yields >75%; lower oligomer yields	[137]
2014	Ferrierite	10 MR (two-dimensional)	8.5	5	Water 260 °C 4 h	10 recycles with: conversion: 90–99%; BUFA yields: 75–85%	[139]

a) Relative to the feedstock.
b) Calcination at 450 °C instead of 550 °C.

The same year, the potential of one-dimensional zeolites with linear large-sized channels (mordenite, omega, and L-type) was confirmed by Roberts *et al.* [128, 129]. Reactions were carried out for 4 h with 1–5% catalyst loading without addition of water. Optimum temperature around 265 °C and minimum Si/Al ratios of 10 were disclosed. Further improvements were obtained by crystal morphology manipulation, such as flat-plate crystals with the pores along the shortest dimension ($L/D > 10$, where L is the crystallite diameter and D is the crystallite thickness); for both mordenite (hexagonal disks) and L-type zeolites (circular plates), BUFA yields above 50 wt% could be reached with 2.5% loading.

In 2004, large-pore zeolites (>6 Å) were claimed to promote OA conversion to BUFA [130, 131]. Reactions were carried out for 5 h at 250 °C with a high catalyst loading (10%). OA conversions of (up to) 50% were disclosed using beta zeolite (three-dimensional, BEA) with Si/Al = 12.5. The oligomeric fraction is not reported in the product composition, and the comparative example is based on mordenite with very high acidity (Si/Al below 10), so the claim cannot be deduced based on the data provided. The patent discloses the application of H-beta zeolite for a wide range of unsaturated fatty acid sources (a.o. tallow oleic acid, erucic acid), while up to this point most studies used only high-purity oleic acid. Zhang *et al.* also described a "one-pot" process of isomerization followed by hydrogenation, catalyzed by Pt or Pd supported on Beta. In addition, intermediate state shape selectivity was used to explain the observed branching pattern [132, 133]: the large pore size results in both ethyl- and methyl-branched fatty acids, while medium pore size limits the branching to methyl. Compared to the clay-catalyzed process, the large-pore zeolites increase the fraction of multiple-branched fatty acids; quaternary carbon atoms, indicative of geminal, doubly alkyl-substituted ISAC, were not detected in the analysis by ^{13}C NMR, however.

OA conversion to BUFA in the presence of beta zeolite could again be improved by the addition of a small amount of water (as earlier with the mordenite) and by optimizing the zeolite calcination temperature [134]. A compromise between template removal and preservation of the strong Brønsted sites was found at 450 °C instead of 550 °C (conversion of 67% vs. 46% after 5 h at 250 °C for Si/Al = 13.5 and a loading of 3%).

Zhang *et al.* also disclosed the use of mesoporous sieves (Mesoporous Aluminosilicate (MAS)-5, Si/Al = 25) for OA conversion to BUFA [135, 136]. After 5 h reaction at 250 °C with 10% catalyst loading, a conversion of up to 60% was achieved. Such structures are believed to further enhance acid site accessibility to the large fatty acid molecules. Again, no details of the oligomeric fraction are reported in the product composition, and its potential increase due to the larger external surface cannot be ruled out. On the other hand, filtration of such mesoporous sieves from the reaction mixture left little residue in the spent catalyst, and deactivation was less marked (OA conversion only decreased from 60% to 44% upon reuse after filtration, acetone washing, and drying).

3.10.4
Ferrierite – a breakthrough in fatty acid isomerization

In 2007, Ngo et al. reported a step change in both OA conversion (>95%) and selectivity toward BUFA (>70%) with protonated zeolites from the ferrierite group [58]. Two commercial ferrierite catalysts ex Tosoh (Si/Al = 8.5, H-Fer-K) and Zeolyst (Si/Al = 27.5, H-Fer-NH$_4$) were used, the former activated by HCl exchange and the latter by calcination at 500 °C. A number of cocatalysts were tested, of which water was found to be the most effective. Reactions were carried out for 6 h at 250 °C with a catalyst loading of 2.5–5%. Comparative examples with clay (2.5 h at 250 °C with a 4.3% loading) and protonated mordenite (Si/Al ∼ 9, 6 h at 250 °C with a 2.5% loading) clearly confirmed the superiority of ferrierite. This zeolite was however found to suffer from deactivation and could not be reused.

Later, the ferrierite selectivity to the monomeric fraction was further improved by the addition of a small amount of a bulky Lewis base as promoter, for example, 2.5% (relative to the catalyst) of triphenylphosphine (TPP) [137]. It is believed that such a base interacts with the non-shape-selective acidic sites on the external zeolite surface. However, this method did not allow the complete suppression of residual oligomers and significantly slowed down the reaction; the temperature was increased to 280 °C to compensate for this effect. TPP also promoted reaction selectivity with mordenite.

Picolinyl esters of the hydrogenated BUFA were analyzed by GC × GC-TOF-MS. Ngo et al. reported that zeolites ferrierite and mordenite gave different branching fingerprints (both type and number of isomers differed) [137]. These results are in line with earlier findings of Zhang et al. [132, 133]. Surprisingly, when analyzing the picolinyl esters of the BUFA, only 30 isomers were counted in the distillate from ferrierite catalysis [138]; this is hardly higher than the 28 species found after hydrogenation [137], suggesting a preferred geometric configuration for the remaining double bonds.

Ngo et al. proposed a series of protocols to regenerate the spent ferrierite, allowing for 10–20 times reuse. After an initial solvent washing, the first method involves a laborious acid treatment that consumes a large amount of water [137]. The second procedure alternates a number of heat (110–260 °C) and acid treatments (after five to six cycles) [139]. The focus of this study was on regeneration, and no details were reported on the deactivation mechanisms themselves. Recently, [140], spent ferrierite catalyst samples obtained from after OA isomerization under similar conditions to Ngo et al. were analyzed by a combination of spectroscopic and characterization techniques to get detailed insight into the mechanism of deactivation. The active sites were shown to be poisoned by (poly)enylic species thought to be formed from hydrogen transfer reactions on the OA. In addition, zeolite pore blockage was detected at very early stages of the reaction, due to the formation of mainly alkyl aromatic species. Importantly, this latter observation suggests that only the pore mouth is actively employed in catalysis.

The relationship between ferrierite structure and activity has also been studied in depth for the OA isomerization reaction [141]; in this work, subtle differences in the morphology and acidity (including type, strength and accessibility of the active site) were shown to lead to significant variations in activity and selectivity to (mono)branching. More specifically, a highly active zeolite for OA isomerization requires low external acidity (to inhibit non-selective reactions such as oligomerization of the OA) and an optimal density of Brønsted acid sites in the 10-MR channels.

The examples described earlier clearly show that zeolites hold considerable promise for the selective manufacture of ISAC. The patent literature bears witness to the research effort of the oleochemical industry in searching for the ideal microstructure. Inspired from the development of zeolites in the refining and petrochemical industry in the 1990s, catalytic testing initially targeted the microstructures with medium to large channels. Ferrierite, extensively researched for its superior activity and stability in the isomerization of butene to isobutene, has only recently been tested in the skeletal isomerization of OA. In this reaction, it has been shown to give complete conversion, and high selectivity to the BUFA, representing a major improvement over previously tested zeolites. The most recent research has provided key insights into the mechanism of the reaction and the origins of deactivation, and highlights how certain elements in the catalyst structure play in a key role in determining activity and selectivity. This new knowledge paves the way to even more effective catalyst designs for alkyl chain branching of lipids, which remains an underexploited reaction in the oleochemical toolkit.

3.11
Summary and Conclusions

Vegetable oils and animal fats are important and established raw materials for the production of chemicals and ingredients. From its origins in the production of stearine candles more than 150 years ago, and shaped by major world events in the twentieth century, the oleochemical industry has grown in scale and diversity to become an important branch of the chemical industry. With increasing emphasis on renewable and sustainable industrial practices, oleochemistry has gained a new momentum as a means to develop alternatives to fossil-derived chemicals and products. In the last decades, research in oil and fats for industrial use has extended beyond the traditional boundaries into areas previously occupied by the food, chemical, and other industries. Three directions in particular can be identified:

- *New lipid sources.* Through crop breeding and agronomics, development of alternative lipid sources from plants, yeasts and algae, and exploitation of existing non-food plant oil sources.

- *Catalysis.* Novel catalysts, including enzymes, adapted for oleochemical feedstocks from other fields of development, to achieve new functional derivatives and expand the range of application of oils and fat-derived chemicals.
- *Biorefinery concepts.* Integration of processes and streams from a wide range of plant-derived feedstocks to achieve the economics and scale of production. This is strongly linked to the above developments but goes further in combining traditionally distinct sources (e.g., wood/cellulose, starches, sugars, plant proteins, etc.) and stimulating new developments in process technology, biotechnology, and catalysis required to achieve a true biorefinery concept.

In this chapter, we reviewed the role of catalysis and catalyst development in the production of ISAC, both from a historical perspective and through recent research into more selective zeolite-catalyzed routes. ISAC holds a unique position in the oleochemical portfolio, due to its special properties, and this has been illustrated through a discussion of the markets and applications where its functionality is particularly valued. As an example of the direction of oleochemical research, it illustrates the potential of proper catalyst design to open up significant new markets and applications for oleochemicals.

Acknowledgments

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