Sustainability That Gets Under the

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Evonik Industries is the only company worldwide that offers biotechnologically produced emollient esters for the cosmetics industry. Compared to the chemical production process, the biotechnological variant boasts extraordinarily good selectivity, mild reaction conditions, and high product purity. It is also sustainable: For the first time, researchers at Evonik have used a life cycle assessment to quantitatively record and evaluate the advantages of biocatalysis on the example of myristyl myristate production.

With a surface area of as much as two square meters and a weight of about ten kilograms, the skin is the largest human organ. It is also the body's control center for a number of sensory perceptions, a key element in the regulation of body temperature, and the protective covering for the body. Care of the skin is a high priority in our society. According to one ongoing study, begun in the early 90s by the German Cosmetic, Toiletry, Perfumery, and Detergent Association in cooperation with various universities and institutes, over 90 percent of women and nearly half of all men in Germany alone regularly use facial creams and body lotions.

But how does the user like his skin to feel? Should the feeling be relaxing, soft, light and silky, or rich and heavy? The decisive factor here is the oil phase, which increasingly consists of "emollient esters." Emollient esters are produced through esterification of a fatty acid with a long-chained alcohol. As the oil phase of an oil-in-water (O/W) or water-in-oil (W/O) formulation, emollient esters, along with emulsifiers and other additives, represent valuable starting products for skin care cosmetics such as creams and body lotions.

A trailblazer in biocatalysis

About 50 different emollient esters are now available on the market for creating creams and lotions for optimal skin feel, depending on preference and application. Evonik currently has about 20 of these esters in its portfolio, and is the sole supplier worldwide which produces four esters in a biotechnological process using custom-tailored enzymes: myristyl myristate, decyl cocoate, cetyl ricinoleate and isocetyl palmitate. With a production volume of several hundred metric tons per year, myristyl myristate is the most important of these.

The biggest advantage of the enzyme catalysts is their mild reaction conditions. The chemical process for the esterification of long-chain fatty acids and fatty alcohols requires temperatures as high as about 240 °C (464 °F), which can generate raw products that are dark-colored and do not meet the required quality criteria for cosmetic products in terms of purity, color, and smell. For this reason, they undergo a host of reprocessing steps in which they are steamed, bleached, and filtered to remove the undesired color and smells caused by the impurities.

The biocatalytic process, on the other hand, runs at 60 °C (140 °F) under nearly physiological reaction conditions, and supplies highly selective ultra-pure, colorless products that obviate the need for expensive, time-consuming reprocessing and cleaning. The only problem: Because the enzyme is extremely expensive, a sufficient number of campaigns must be carried out each time the enzyme is loaded to make the process cost-effective compared to the chemical variant. Because the enzyme is by nature highly sensitive, it cannot be used in its natural state.

To find an economically sensible solution, Evonik is using immobilized enzymes, a variant in which the enzyme is bonded to small spheres that act as a carrier material. Immobilization allows the enzymes to be integrated into a fixed-bed reactor with a circulation loop, through which the reaction charge is pumped long enough to reach the intended yield. With this technique, the biocatalyst remains stable longer, and can be separated more

Skin

Powerful quartet – the emollient esters produced in an enzymatic process at Evonik

- Myristyl myristate: Ester of myristic acid with myristyl alcohol. White, wax-like substance. Used as an easily spreadable oil component in O/W emulsions, especially in lotions, and to improve the consistency of W/O emulsions
- Decyl cocoate: Ester of coconut fatty acid with decyl alcohol. Primarily used in face care products and in O/W-type sunscreen formulations
- Cetyl ricinoleate: Ester of ricinoleic acid with cetyl alcohol. Uses include, for example, skin care products, decorative cosmetics and lipsticks
- Isocetyl palmitate: Ester of palmitic acid with isocetyl alcohol. Used, for example, as a substitute for mineral oil in skin care products, especially for dry skin

easily from the reaction mixture – a technological advancement that explains why Evonik is now the only company that offers enzymatically manufactured emollient esters.

Disproportionate growth in the market for natural cosmetics

Bioproducts are on the rise, and not only in the food industry. In Europe, the market for natural cosmetics is recording double-digit growth rates. Even though bioproducts are still a niche market, L'Oréal, the world's largest cosmetics corporation, recently acquired the natural cosmetics chain The Body Shop, and even discount chains are attaching great importance to environmental products. The reason is the consumer's growing desire for natural products, which are also often labeled as such.

Biotechnologically produced emollient esters meet this demand. This is also clear from the fact that, when given a choice between an emollient ester produced in the conventional way and one produced enzymatically, more and more cosmetic companies are choosing the latter.

Life cycle assessment confirms sustainability of biocatalysis

The life cycle assessment shows that what the consumer wants is also good for the environment. In collaboration with the Danish company Novozymes A/S, the Consumer Specialties Business Unit of Evonik conducted the first environmental life cycle assessment (LCA) of an emollient ester for cosmetic applications. The researchers selected production of the emollient >>>

Figure 1. Using the production of myristyl myristate as their model, Novozymes and Evonik are the first companies to conduct an environmental life cycle assessment for both the enzymatic and chemical manufacture of an emollient ester for cosmetics

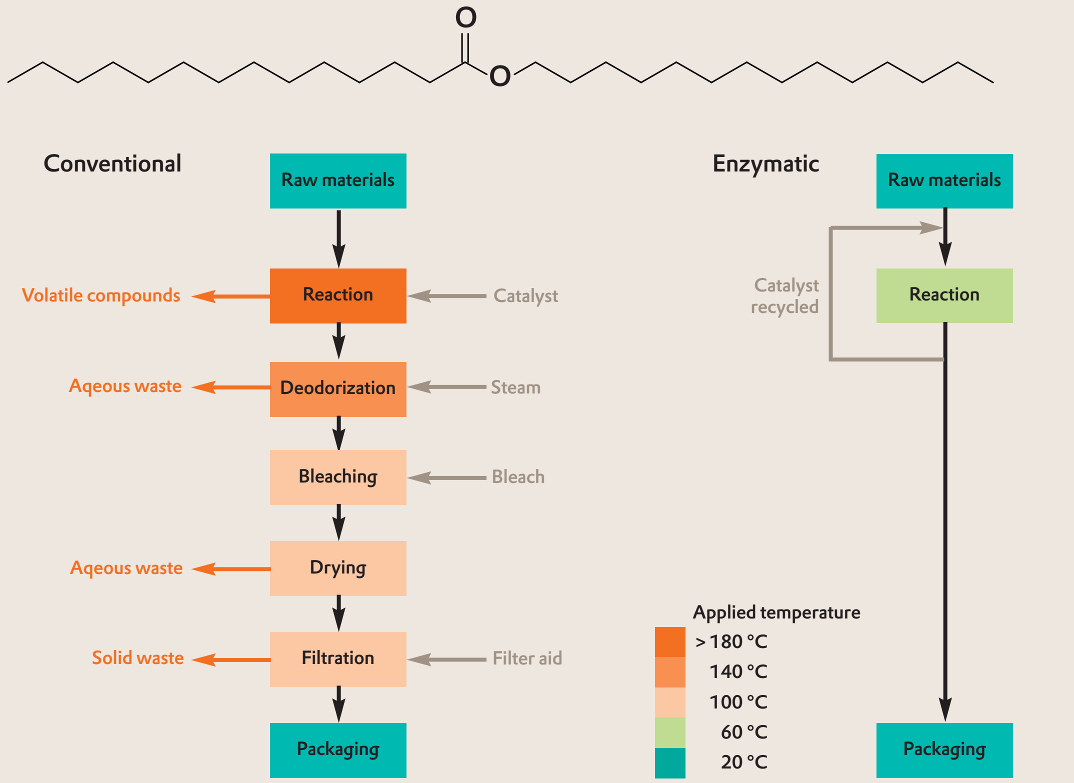
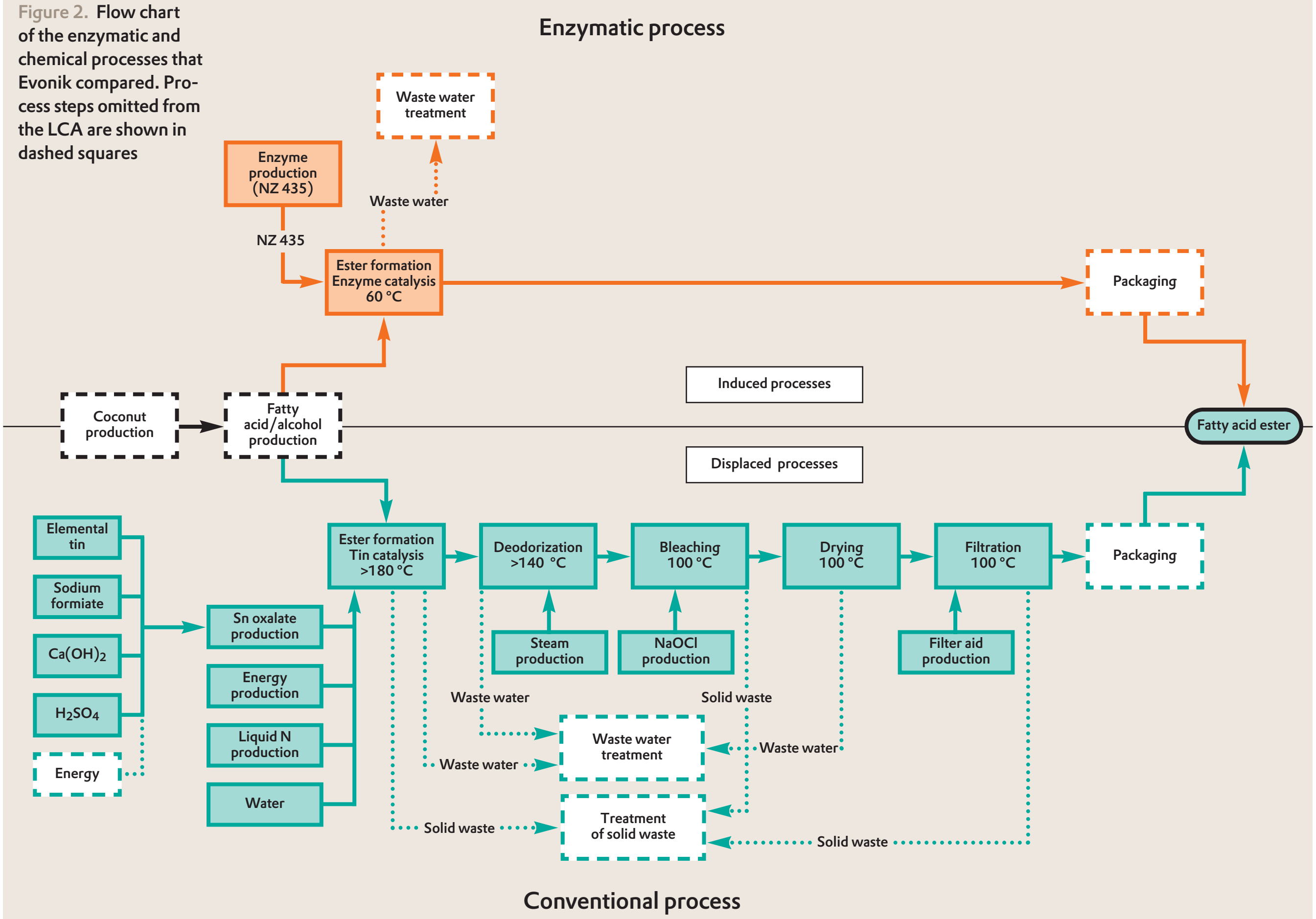


Figure 2. Flow chart of the enzymatic and chemical processes that Evonik compared. Process steps omitted from the LCA are shown in dashed squares



ester myristyl myristate as their model process, but the results can be easily transferred to similar cosmetic fatty acids (Fig. 1).

In their assessment, the scientists used immobilized lipase B from the organism *Candida antarctica* to examine the industrial enzymatic process used at Evonik to produce the ester, including recovery of the enzyme, all the way to its deactivation. They then compared this process with the conventional chemical production process, which is carried out at 240 °C (464 °F) and uses tin oxalate as catalyst. Other parameters for this variant included the use of nitrogen as inert gas, and a refinement process consisting of bleaching with sodium chlorite, three hours of steam stripping, and filtration.

Scientists made out an inventory for both processes, calculating how much electricity was needed for stirrers and pumps, how much energy is needed to heat the vessel, what raw materials in what quantities go into the process, and what kinds of waste are produced. In those few cases in which the parameters in the detailed analysis are based on assumptions or are difficult to calculate, the most conservative variant was used to avoid giving the advantage to the enzymatic process. For example, the life cycle assessment did not consider all waste treatment, although the enzymatic process would have a clear advantage here owing to the significantly lower amounts of waste it generates. The higher yields of the enzymatic process were, therefore, completely disregarded in the life cycle assessment (Fig. 2).

The result of this inventory was an inventory table that lists the raw materials and energies used, and the wastes generated from all the process steps. They then integrated the existing life cycle assessments contained in databases for the raw materials used. This was the only way they could ensure that the life cycle assessment factored the energy and raw material consumption of myristyl myristate production as well as the production of the feed materials (Fig. 3).

If no life cycle assessment was available for a starting material, the researchers traced the product lines based on the starting material until data was available. They had to rely on this method in the case of tin(II) oxalate, the catalyst for the chemical process, because there is no life cycle assessment for it. Instead of tin(II) oxalate, they used elemental tin, sodium formiate, calcium hydroxide, and sulfuric acid as starting materials, and produced calcium sulfate as the waste product. Energy consumption for the production of tin(II) oxalate was completely disregarded – a conservative assumption to avoid giving the advantage to biotechnology. The scientists were also unable to find a life cycle assessment for sodium chlorite, so they got around the problem by substituting sodium hypochlorite.

Using the individual life cycle assessments of all the starting materials, the scientists evaluated both processes based on five standardized environmental categories: energy consumption, influence on global warming using greenhouse gas emissions, acidification of soil through noxious gases such as SO_2, the eutrophication of soil and water through the immission of nutrients such as phosphorous and nitrogen, as well as smog formation through volatile organic compounds.

The results speak loud and clear: Despite conservative assumptions, the biocatalytic manufacturing process for the emollient ester myristyl myristate can, on balance, save more >>>

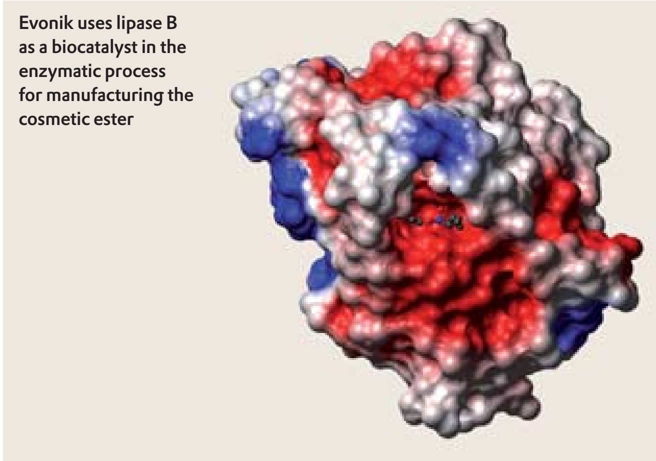


Figure 3. **First, the researchers listed the used raw materials, energies, and wastes generated from all the process steps in the comparison in an initial inventory table (upper table). To make a total assessment, their next step was to integrate the individual life cycle assessments of the raw materials and prepare a second inventory table (lower table)**

		Conventional	Enzymatic
Electricity (primary energy)	GJ	0.63	2.38
Heating energy (from electricity)	GJ	6.34	0.76
Gaseous nitrogen	Litres	3,200	
Tin(II)oxalate	kg	25	
Novozyme 435	kg		0.27
Filter aid (Tonsil)	kg	25	
Bleach $NaOCl_2$	kg	20	
Water for steam	kg	105	
Cooling water	kg	570	
Waste water	kg	445	180
Tin-containing waste	kg	70	
Enzyme waste	kg		0.5

		Conventional	Enzymatic
Total energy from electricity	GJ	6.97	3.14
Liquid nitrogen	kg	5	
Tin from mining	kg	14	
Sodium formiate	kg	17	
H_2SO_4, 96 %	kg	18.2	
$Ca(OH)_2$, solid	kg	9.3	
Novozyme 435	kg		0.27
NaOCl, 15 %	kg	133	
Waste $CaSO_4$	kg	17	
Tin-containing waste	kg	70	
Enzyme waste	kg		0.5

Figure 4. **The results of the life cycle assessment show that the enzymatic process is considerably more eco-friendly**

Results of the life cycle assessment 5 ton scale		Conventional	Enzymatic	Savings %
Energy	GJ	22.5	8.63	62
Global warming	kg CO_2 eq.	1,518	582	62
Acidification	kg SO_2 eq.	10.58	1.31	88
Nutrient enrichment	kg PO_4 eq.	0.86	0.24	74
Smog formation	kg C_2H_4 eq.	0.49	0.12	76

Figure 5. **In the chemical process the use of tin and the energy necessary for heating the reaction vessel have the biggest impact on the environment**

Main contributors to environmental impact	Fossil energy %	Global warming %	Acidification %	Nutrient enrichment %	Smog formation %
Tin	15	15	70	55	45
Heating energy	70	70	20	35	40
NaOCl	5	5	5	5	5
Sodium formiate	< 1	< 1	< 1	< 1	1
Filter aid	2	< 1	< 1	5	1

than 60 percent energy while reducing the formation of environmentally damaging impurities by as much as 88 percent (Fig. 4). All these facts clearly support the sustainability of the biocatalytic process.

Finally, in their quest for improvement potential, the scientists analyzed which process steps and which feed materials have the biggest environmental impact in chemical synthesis (Fig. 5). They determined that the leading energy consumer is the heating of the reaction vessel, which also makes the chief contribution to the greenhouse gas effect. Tin was found to have the most environmentally damaging impurities.

Portfolio of enzymatically manufactured products will continue to grow

Evonik is encouraged by the positive response of cosmetics manufacturers to products manufactured with enzymes, and plans to market more high-quality enzymatically manufactured products for the cosmetics industry. In cooperation with the marketing department of the Personal Care Business Line, researchers are identifying new target compounds, and studying their production and technical application properties.

Because of the intrinsic advantage of biocatalysis – high selectivity and mild reaction conditions – and the opportunity to exploit both the environmental and economic improvement potentials in the pursuit of sustainability, researchers in the Consumer Specialties Business Unit are also working on the enzymatic synthesis of products for other fields of application. Even though enzymes currently reach their limits when it comes to certain substrates – for example, in the case of emollient esters from branched carboxylic acids, which enable the production of ultra-light creams – they keep their promises to consumers and chemists. They produce high-purity substances, protect the environment, and open the door to new products – all good reasons for the Evonik researchers who work in this area to press on with their work, and continue expanding the company's range of biotechnologically manufactured products. They laid the foundation for this work years ago, having built a broad enzymatic technology platform with numerous patents that open up access to new substance classes.

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Oliver Thum is head of biotechnological research in the Consumer Specialties Business Unit of Evonik. After studying chemistry at the University of Bonn, where he finished his thesis under the direction of Prof. Wilhelm Boland of the Max Planck Institute for Chemical Ecology in Jena, and subsequently earned his doctorate, he began his professional career in 2002 as a scientific assistant at Noxxon Pharma AG in Berlin. One year later he moved to Evonik Industries as group leader in research and development in the Consumer Specialties Business Unit. Thum has held his current position since 2006.
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