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Biocatalysis – A Sustainable Method for the Production of Emollient Esters

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■ Introduction

The biocatalytic production of chemicals, also knows as »white biotechnology«, has gained much attention within the last years (1,2). The generally perceived advantage of this technology is due to the intrinsic properties of enzymes that distinguish them from conventional catalysts: First of all they usually show a high selectivity, yielding products with high contents of desired active material. Secondly they act at comparably mild reaction conditions, such as temperatures at around or slightly above room temperature, at more or less neutral pH values, etc. These features can lead to simple production processes, yielding products of superior quality without the need for multi-step synthesis or harsh reaction conditions that can be sometimes found for conventional organic chemistry.
Biotechnology has already arrived in the field of cosmetic raw materials. Quite famous and obvious for example is the synthesis of complex active ingredients, such as ceramides, by biotechnological processes. But even relatively simple cosmetic ingredients, such as emollients based on fatty acid esters, can advantageously be made by enzyme catalysis. Recently, the advantages of the biocatalytic production of such esters have been demonstrated with respect to product quality and process simplification compared to conventional, chemical catalyzed processes (3).
Another general perception is the sustainability of biocatalytic processes due to the above mentioned mild reaction conditions. But to our knowledge this assumption has only be proven for a very few cases within chemical industry and never been quantified for a synthesis process related to cosmetic industry.
The proper tool to analyze the environmental impact of production processes, especially when comparing two related processes, is the Environmental Life Cycle Assessment (LCA). Even though some remarkable efforts have been undertaken recently to proof the general environmental benefits in broad studies, such as the BREW study (4), investigations on concrete products still remain to be pursued. Even more, beside the knowledge on critical product parameters such as quality aspects a detailed knowledge on reaction parameters for conventional processes as well as for biotechnological ones is necessary to perform a LCA study on sound data.

■ Materials and Methods

The LCA method, which is a generally accepted method for assessing the environmental impact of chemical processes throughout the entire lifecycles, provides a profound basis for choosing the environmentally most attractive process from a number of alternatives. The current assessment is in agreement with the ISO 14040 requirements and is based on the principles described by *H. Wenzel* et al (5). The modeling has been facilitated in SimaPro 6.0 LCA software, and the study has been externally critically reviewed by an independent and acknowledged reviewer.
The assessment evaluates the systems to be compared in terms of consumption of resources and emissions to the environment. The emissions are translated into potential contributions to standardized environmental impacts. As in most studies, we considered the following five impact categories, which are all standardized according to ISO:

- Energy consumption (MJ energy carrier)
- Global warming potential (kg CO_2-equivalents)
- Acidification potential (kg SO2-equivalents)
- Nutrient enrichment potential (kg PO_4-equivalents)
- Smog formation potential (kg ethylene-equivalents)

Equivalence factors for compiling the individual contributions to the environmental impacts are derived from Eco-indicator 95 V2.1.
As model process served the production of myristyl myristate, a frequently used emollient ester, but the results obtained can be easily transferred to all similar cosmetic esters derived from fatty acids. Two production procedures have been compared: On the one hand the enzymatic production using immobilized Lipase B from *C. antarctica* (Enzyme) under real industrial conditions as currently applied at a site of Evonik Goldschmidt, including recycling of the enzyme until deactivation. On the other hand a state-of-the art conventional process based on tin(II) oxalate as catalyst at 240 °C, like it is widely used in the synthesis of cosmetic esters. We defined usual quality specifications for such kind of products,

especially with respect to content of active material, color and odor. To obtain a product of such quality by the chemical process we assumed the use of nitrogen as inert gas and a downstream refinement process, consisting of bleaching with sodium chlorite, three hours of steam stripping and final filtration with the addition of a filter aid. Electricity needed for stirrers and pumps was calculated by using their power input, heating energy needed to heat up the vessel and the raw materials has been calculated by available physical-chemical data and based on real-life data.
Because the data used for the assessment are taken from actual plant processes we consider the results to be more valuable than data obtained from optimized, but theoretical scenarios.
When carrying out the assessment process we started with a deep and careful analysis of the two processes and all the steps involved from cradle-to-gate. Mostly, appropriate data could be obtained from databases. In those few cases when the impact of process steps or used chemicals was not contained in the existing databases assumptions had to be made on the unknown parameters. This has been done highly conservative in order not to give any unjustified advantage to the enzymatic procedure. Furthermore, benefits of the enzymatic process such as higher yield and better quality of the obtained products have not been considered in the assessment and will be treated as additional benefit, even though the impact of these benefits is considered to be significant.

■ Results

Performing all necessary data collecting and calculation the inventory table, usually recognized as heart piece of an LCA **(Table 1)** was prepared. This table includes all production steps, used raw materials, energy, produced waste, etc. for both processes to be compared. Disregarding the above mentioned higher yields of the enzymatic processes further allows us to assume the use of the same amounts of raw materials and thereby disregarding their environmental impact, including transportation and production.

Next step was the transformation of the results from this first inventory table to such ones, where precise environmental data can be found in databases due to previous calculations of LCA. Using the above mentioned guidelines of conservative assumptions we replaced the used chemical catalyst tin(II) oxalate by the ultimate raw materials used for its production. We assumed a 100% yield on this process and complete recycling of all used aids as well as of all wash waters. Furthermore we disregarded any energy use for this energy-consuming process. This allowed us in total to replace 25 kg of tin(II) oxalate with 14 kg of elemental tin, 17 kg sodium formiate, 9.3 kg calcium hydroxide and 18.2 kg H_2SO_4 (96%); additionally, 17 kg of $CaSO_4$ will be produced as waste.
Like for the tin(II) oxalate we were not able to find appropriate data in databases for the sodium chlorite. Therefore we modeled it with sodium hypochlorite, which is actually a raw material for the production of sodium chlorite, again giving a conservative assumption and disregarding any need of energy for this process.
Another important topic for the LCA is the waste treatment. Unfortunately it is not easy to calculate this as it depends much on the methods how the waste is treated at the plant. As it quite obvious from **Table 1** that the conventional process produces much more waste - waste water as well as problematic solid waste such as tin containing filter material – we decided to disregard the whole waste issue, knowing that this is a highly conservative assumption favoring the conventional process. All these calculations and transformations lead to the final inventory table as it can be seen in **Table 2**.

		Conventional	Enzymatic
Electricity	(primary energy, GJ)	0.63	2.38
Heating energy	(from electricity, GJ)	6.34	0.76
Gaseous nitrogen	(liters)	3200	
Tin(II) oxalate	(kg)	25	
Enzyme	(kg)		0.27
Filter aid	(Tonsil, kg)	25	
Bleach: NaOCl2	(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

Table 1 Inventory table for the production of myristyl myristate on 5 ton scale

		Conventional	Enzymatic
Total energy from electricity	(GJ)	6.97	3.14
liquid nitrogen	(kg)	5	
Tin from mining	(kg)	14	
Sodium formiate	(kg)	17	
H2SO4, 96%	(kg)	18.2	
Ca(OH)2, solid	(kg)	9.3	
Enzyme	(kg)		0.27
NaOCl, 15%	(kg)	133	

Table 2 Final inventory table for the LCA

After finishing the inventory table both processes can be visualized by a flow scheme, illustrating both processes (**Fig. 1**). As can be seen in the figure all relevant process steps are given and those who have been disregarded for the LCA due to the reasons mentioned above are represented by dashed squares.

After preparing all necessary data for the inventory table the environmental impact of all its entries has been calculated as described above and visualized using the five defined key parameters energy consumption, global warming potential, acidification potential, nutrient enrichment potential, and smog formation potential, the results can be seen in **Table 3**.

More detailed it can be shown that the energy consumption of the enzymatic process (8.63 GJ equivalents of fossil energy resources, gas was used as model energy carrier) is significantly lower than that of the conventional process (22.5 GJ), resulting in energy savings of 13.87 GJ, when replacing a conventional with a biocatalytical process. Analogously, huge savings in the other four categories (964 kg CO_2, 9.82 kg SO_2, 0.62 kg PO_4, and 0.37 kg VOC, respectively) become apparent, of which the savings in CO_2 are most important beside those in used energy resources regarding the absolute numbers.

In summary it can be shown that the use of energy can be reduced by more than 60% and the formation of unwanted pollutants by up to 90%. This approach gives maybe the most impressive view on the results regarding the sustainability of white biotechnology and on its direct impact to the environment.

		Conventional	Enzymatic	Savings
Energy	GJ	22.5	8.63	62%
Global warming	kg CO2 eq.	1518	582	62%
Acidification	kg SO2 eq.	10.58	1.31	88%
Nutrient enrichment	kg PO4 eq.	0.86	0.24	74%
Smog formation	kg C2H2 eq.	0.49	0.12	76%

Table 3 Impact on the defined five environmental key parameters

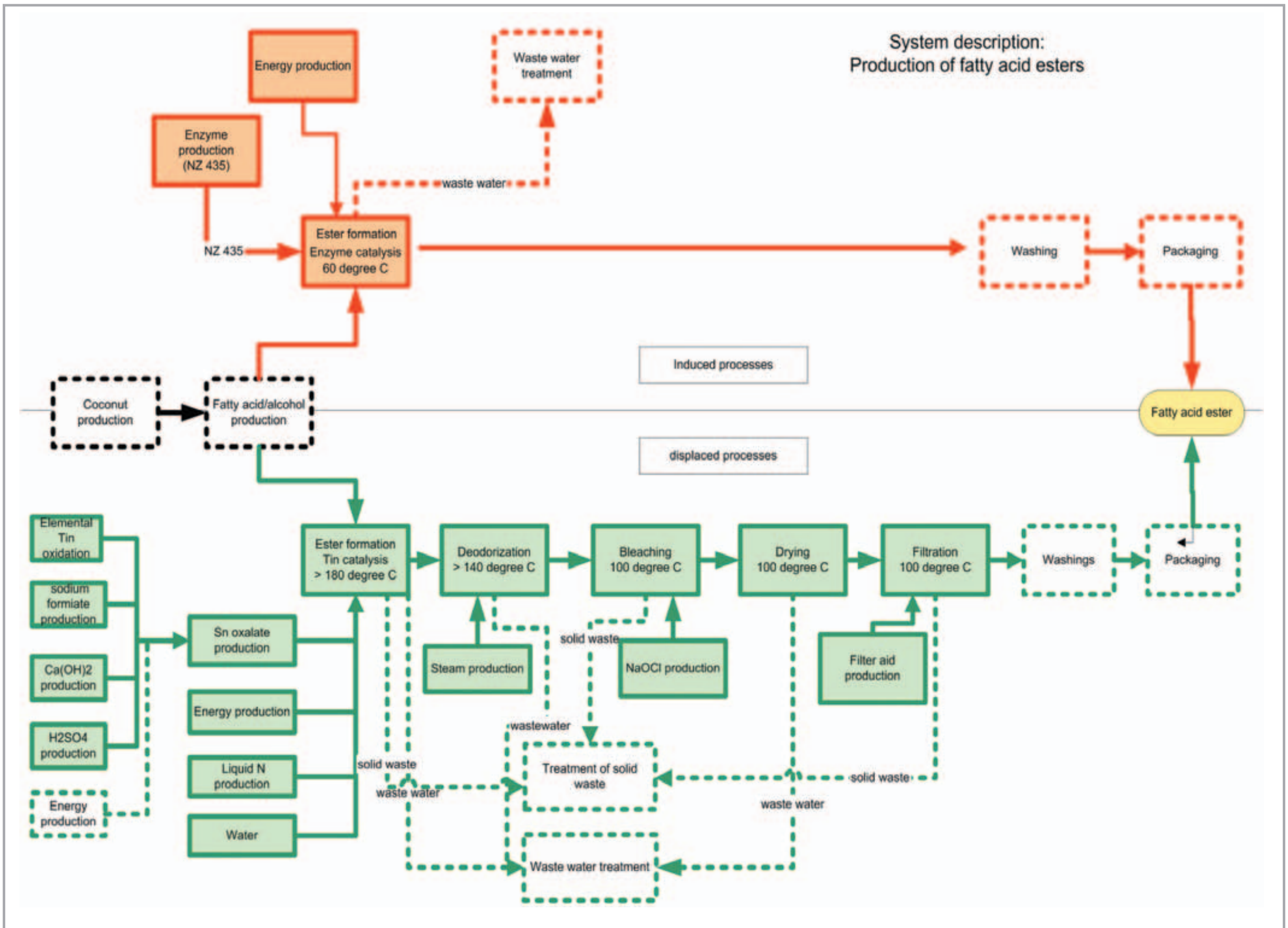

Fig. 1 Flow scheme of the two processes compared; the enzymatic process (above) and the conventional one (below). Process steps omitted from the LCA are given in dashed squares.

	Fossil Energy	Global warming	Acidification	Nutritient 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%

Table 4 Major contributors to each environmental key parameter

Finally, we investigated which steps are the most important ones, i. e. which have the biggest impact on the five environmental key parameters. This allows an easy estimation on the effect modifications of the production processes would have (e. g. using less catalyst, savings in energy, etc.). As can be seen from Table 4 the use of elemental tin and the energy necessary for heating the vessel are the two dominating factors; the first having the biggest impact on the acidification, eutrophication and smog formation, the latter on the use of energy resources and greenhouse effect.

Discussion

The performed cradle-to-gate analysis easily shows that the biocatalytical process is significantly more eco-friendly than the conventional one in all categories analyzed. Energy consumption is reduced by more than 60% and the emission of unwanted pollutants is reduced by up to 90%. We have therefore been able to give a concrete proof for the widely spread assumptions of the environmental benefits of enzyme catalyzed processes in this particular case. We have chosen and investigated the production of the emollient ester myristyl myristate as a model reaction, but the results can of course be easily translated into the production of any other fatty acid based emollient as we know that the differences in producing them are marginal for the enzymatic as well as for the chemical catalyzed processes. These results are even more impressive as they have been achieved making a lot of assumptions that favor the conventional process, such as not including the waste treatment issue. By determination of the major contributors to the overall effect it could be shown that only the use of tin and fossil energy resources has a significant effect, whereas all other parameters, such as bleaching and the use of filter aid can be disregarded when comparing such processes with respect to their environmental impact. In conclusion, the enzymatic production of such kind of products can be considered to be a prime example of a sustainable process.

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