Review TRENDS in Biotechnology Vol.25 No.3

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Industrial biotechnology for the production of bio-based chemicals – a cradle-to-grave perspective

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Shifting the resource base for chemical production from fossil feedstocks to renewable raw materials provides exciting possibilities for the use of industrial biotechnology-based process tools. This review gives an indication of the current developments in the transition to bio-based production, with a focus on the production of chemicals, and points out some of the challenges that exist in the large-scale implementation of industrial biotechnology. Furthermore, the importance of evaluating the environmental impact of bio-based products with respect to their entire life cycle is highlighted, demonstrating that the choice of the raw material often turns out to be an important parameter influencing the life cycle performance.

Introduction

Chemistry has had, and continues to have, a fundamental role in almost every aspect of modern society. Despite providing us with a vast array of useful products, the chemical industry has been subjected to close scrutiny owing to concerns about its reliance on fossil resources, its environmentally damaging production processes, and the production of toxic by-products, waste and products that are not readily recyclable or degradable after their useful life. The industry has come under increasing pressure to make chemical production more eco-friendly. Governments across the globe are increasing the fines levied for pollution, the costs of waste disposal, and penal taxation for the storage of large quantities of dangerous chemicals. In the EU, new chemical legislations are being introduced, to improve the levels of protection of human health and the environment from chemical risks. For example, the recently proposed REACH (registration, evaluation and authorization of chemicals; http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm) regulatory framework demands registration and safety testing of all produced or imported chemicals. A more product- or sector-related legislation, such as the Restriction on Hazardous Substances (RoHS) [1], prohibits or severely restricts the use of most dangerous chemicals in electronic and electrical equipment. The sustainability of the chemical industry thus calls for a business strategy that integrates social, safety, health and environmental benefits with the technological and economic objectives of its activities.

The concept of 'green chemistry' was introduced in the early 1990s by the US Environmental Protection Agency (http://www.epa.gov/), in order 'to promote chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products'. Its guiding rule is prevention rather than cure. Green chemistry is currently associated with the 12 principles formulated by Paul Anastas and John Warner [2], which advocate a decrease in the environmental impact of a chemical product by considering aspects of its entire life cycle – from raw material to product use and fate. Examples of these are using renewable feedstocks, selective catalysts and alternative, non-toxic solvents; high atom efficiency; minimizing risks, waste generation and energy consumption; and design of safer and biodegradable chemicals. These principles have since been supplemented by the 12 principles of green engineering, which provide a structure to create and assess the elements of design relevant to maximizing sustainability [3].

In view of the above, this review highlights the current trend towards the bio-based production of chemicals and the potential of industrial biotechnology to provide the process tools to achieve this. Furthermore, it stresses the need for evaluation of the environmental impact of the products from a life cycle perspective. We have chosen to mention only briefly the production of biofuels because this is already extensively dealt with in several reports; however, it should be understood that the two sectors are closely related and can also be synergistic.

A shift from fossil to bio-based raw material

Currently, the products made from bio-based raw materials represent only a minor fraction of the output of the chemical industry. The efforts to shift the prime resource base of the industry from non-renewable to renewable feedstocks have recently gained momentum, primarily because of the rapid rise in the costs of mineral oil and an increasing concern about the depletion of these resources in the near future. The world production of plant biomass is vast and is more than enough to match the demand for the co-production of chemicals, materials and

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Available online 17 January 2007.

www.sciencedirect.com 0167-7799/$ – see front matter doi:10.1016/j.tibtech.2007.01.001

fuels with the demand of foods and feeds [4]. Optimal use of agricultural productivity, agricultural and forest residues, waste biomass, and currently non-used land should enable the further expansion of the bio-based industry, provided the technological and economic limitations are overcome. The growing of dedicated crops for non-food production and breeding, to increase the yield performance of useful plants, is already practised on large scale [5]. Furthermore, the ability to alter the composition of the raw material, either by traditional breeding methods or by molecular biology, has no parallel in petroleum refining.

A change in the feedstock from hydrocarbons to biological molecules will, of course, radically alter the technological basis of the industry. Primarily, there is a need for technologies that enable the economical processing of complex biomass, particularly crop residues and wastes – the production of bioethanol from lignocellulose is one example. Here, the main barrier is the hydrolysis of the cellulose to sugar, which is traditionally accomplished by acid hydrolysis; however, enzymatic hydrolysis provides advantages, including increased yield [6]. Iogen, a Canadian biotech company (http://www.iogen.ca/), has been running an experimental plant since 2004 that uses the enzymatic hydrolysis of lignocellulose, in a process free of fossil fuel. Although the available cellulose raw material is estimated to be enough to replace 40% of the gasoline used in the US, the costs still need to be reduced (e.g. by improving enzyme efficiency through genetic engineering). The availability of inexpensive bioethanol should subsequently promote its use as a precursor for other organic molecules in the chemical industry. For example, ethylene – which forms the backbone of several products, including ethanol, in the petrochemical industry – could be made, instead, by dehydration of ethanol manufactured by the fermentation of carbohydrate feedstock [4]. Hence, directing innovation and technological development from the perspective of a sustainable bio-based society remains a major challenge for the chemical industry. A good starting point is to link the production of chemicals with the rapidly emerging bio-energy industries, from which important bioplatform molecules, including glycerol (from a by-product in biodiesel production), bioethanol and biobutanol (through new process developed by BP–DuPont [www2.dupont.com/Biofuels/en_US/]), will become available.

In moving towards the realization of a bio-based production, the concept of a biorefinery, analogous to the petroleum refinery, has emerged, where the processing facilities based on different technologies are centred on an agricultural (or forest) base, and the biomass is converted into various biochemical and chemical intermediates that are fed into a variety of downstream product lines [7]. By producing multiple products, a biorefinery can take advantage of the natural complexity and differences in biomass components and intermediates and, hence, maximize the value derived from the biomass.

Industrial biotechnology – linking green chemistry and bio-based production

Biotechnology has attracted a great deal of attention as a potentially important tool in facilitating the paradigm shift from fossil to bio-based production, as illustrated in Figure 1. Industrial biotechnology, also known as 'white biotechnology' in Europe, relies on the use of whole cells or enzymes as catalysts, and such processes are already used for the manufacture of several commodity and speciality chemicals [8]. Biocatalysis has more commonly been directed towards the production of high-value products for the fine chemicals and pharmaceutical industries [9–11]; according to a recent survey, 22 out of 38 large-scale asymmetric syntheses already incorporate biocatalysis [12]. The production of chemicals using industrial biotechnology is often able to meet several of the green chemistry principles, particularly reduced energy consumption and waste generation, selective catalysis, and biodegradable products. Furthermore, it can replace multi-step chemical synthesis with a single step involving low energy and less material input [13], and even enables the synthesis of products that are not possible chemically. Organic synthesis using biocatalysis has been possible by performing reactions in predominantly water-free media, or in water–organic biphasic systems [10,14,15]. Owing to concerns regarding volatile organic carbon emissions, there is a development towards replacing the organic solvents used as reaction media with alternatives such as supercritical carbon dioxide and ionic liquids [16,17] or, preferably, solvent-free media.

Recent advances in genomics, proteomics and bioinformatics provide access to an enormous information base for facilitating the choice of suitable microorganisms and enzymes for bioconversions. Engineering of metabolic pathways in microorganisms enables the production of many of the platform chemicals used in the industry, for example, 1,3-propanediol, succinic acid and butanol [18]. New biocatalysts are being discovered by studying novel microorganisms isolated from, for example, extreme

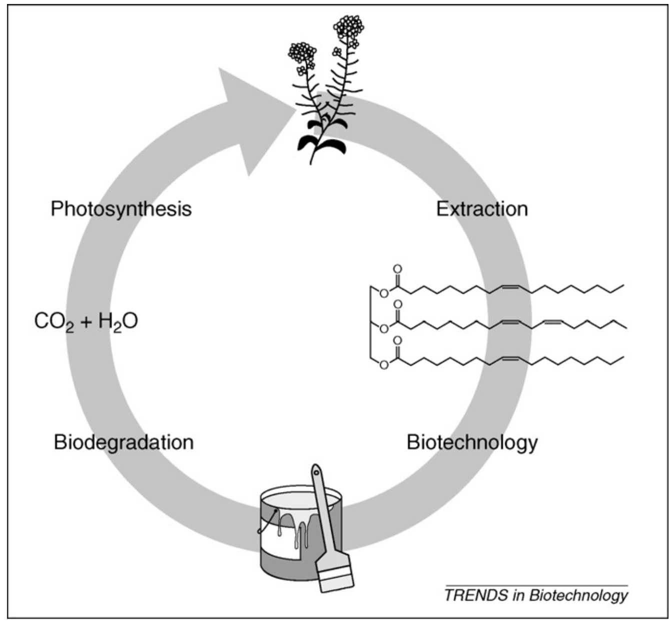

Figure 1. A closed cycle of production of biodegradable chemicals from renewable feedstocks using industrial biotechnology. The products containing such chemicals are environmentally benign in comparison with the products made from fossil feedstocks using end-of-pipe technologies (i.e. those that lead to non-biodegradable products and wastes). The bio-based chemicals can be biodegraded into carbon dioxide and water, which are used during photosynthesis for the production of plant biomass. An example of an oleochemical product made using industrial biotechnology for an application in paints is shown.

environments [19] and also by using metagenomics [20]. Evolution of these enzymes to suit a particular process has further been possible *in vitro*, at substantially higher rates than achieved in nature [21,22]. Furthermore, the development of both high-expression production organisms and suitable cultivation strategies for enzyme production has shown potential for their availability at reduced costs. The advances made by Genencor (http://www.genencor.com/) and Novozymes (http://www.novozymes.com/en) in reducing cellulase production costs and improving performance provide good examples for the use of biotechnology to improve biocatalysis for biomass hydrolysis, which could be an important enabler for the bio-based products industry (Box 1) [23].

The chemical industry in Europe, which contributes ~28% of the demand for chemicals in the world, has identified industrial biotechnology as a key emerging technology area (http://www.suschem.org/) [24]. The share of biotechnological processes in the production of various chemical products is expected to rise from the current level of ~5% to 20% by 2010. The greatest impact will be on the fine chemicals sector, where up to 60% of the products might be based on biotechnology within this time frame [13,25].

In a bio-based production, industrial biotechnology also interfaces with plant biotechnology (green biotechnology), where gene technology is applied to accelerate the process of plant breeding for crop improvement or for altering the composition of the feedstock for a desired product. For example, efforts are made to meet the demands for tailor-made oils and fats by increasing the content of individual fatty acids or the introduction of a new fatty acid. 'High oleic' soybean and 'high lauric acid' rapeseed have been developed already by genetic engineering [26].

A cradle-to-grave perspective for sustainable production

Although industrial biotechnology is intuitively associated with cleaner chemistry and cleaner industrial processes, in most cases these benefits have not been comparatively weighted against the overall inventory of materials and energy required to generate a given product. Hence, when switching from fossil feedstocks and chemical production processes to renewable feedstocks processed with biotechnological methods the assessment of the environmental and economic benefits provided by the process should cover the entire life cycle (cradle-to-grave) of a product – raw material production, manufacture, product use and fate [27]. The major elements of the environmental assessment include primary energy use, raw materials use, emissions to all media, toxicity, safety risk and land use [28]. The significance and relative importance of the different factors with respect to the environmental impact has been assessed [29] using a method that is usually referred to as a life cycle assessment (LCA).

First developed ~30 years ago, the LCA is now a valuable tool in the chemical industry [28,30]. It is used to compare and benchmark the performance of a product against several competing, alternative processes and products, and to find hot spots in the life cycle that might require performance improvements. Figure 2 shows the different improvements that can be made at different stages in the life cycle from a green chemistry perspective. LCAs are also used in industry for strategic planning and marketing purposes [28,30]; many eco-labels and environmental product declarations (EPD) are based on LCAs. In the eco-efficiency analysis used by BASF, equal weight is given to the LCA as to the costs of the product, which include the costs during the production, the usage, and for the disposal or recycling of the spent product [28].

Compared with the number of LCA studies of conventional chemical processes and products, the number of LCA studies that evaluate bioprocesses and bio-based chemicals with respect to environmental and economical benefits is rather limited [30,31], even if the need has been increasing recently. The few studies reported so far have shown that the principle of using renewable feedstock is not necessarily favourable in all situations and for all environmental aspects [31]. By its nature, the use of renewable raw materials gives rise to several specific problems, such as the use of a dedicated crop for manufacture – where the various potential feedstock crops have their own specific characteristics and different environmental performances. For example, the environmental impact of annual feedstock crops using large amounts of chemical fertilisers and pesticides is normally much higher than the impact of perennial crops or annual crops using limited amounts of agrochemicals. The choice of feedstock crop and cultivation system will also affect the long-term soil fertility and biodiversity [32].

The need to include the viewpoint of competing land-use options in the LCAs of green chemicals has been highlighted [33]. For example, a competing land-use option to the cultivation of crops for chemical production might be the cultivation of dedicated energy crops for replacing fossil fuels, which, potentially, could be a more efficient way to reduce the emissions of greenhouse gases. A careful approach, including comprehensive analyses of the various biomass feedstock options and alternative usage opportunities, should be applied, to find the best options for green

Box 1. Challenges that lie ahead for industrial biotechnology in bio-based production

Industrial biotechnology is a multidisciplinary technology based on microbial, plant or animal cells, or their components or enzymes, as catalysts. It includes the integrated application of disciplines such as biochemistry, microbiology, molecular genetics and process technology to develop useful processes and products. Several technological and implementation barriers need to be overcome before its full potential can be realized in the chemical industry.

- Development of novel and improved biocatalysts for the processing of biomass and production of chemicals.
- Development of effective tools and techniques for rapid screening of biocatalysts with desired functions and properties.
- Cost-effective production of biocatalysts by developing efficient high-expression hosts and suitable cultivation technology.
- Improving technologies for bioprocesses (e.g. multiphase reactors and solvent-free reactions) and subsequent product recovery.
- Integration of biotechnology with chemical processes.
- Quantifying and valuing the real environmental and economic benefits of the processes.
- The demonstration of case studies.
- Communication with the important stakeholders, including producers of renewable feedstock and producers and users of the affected chemicals.

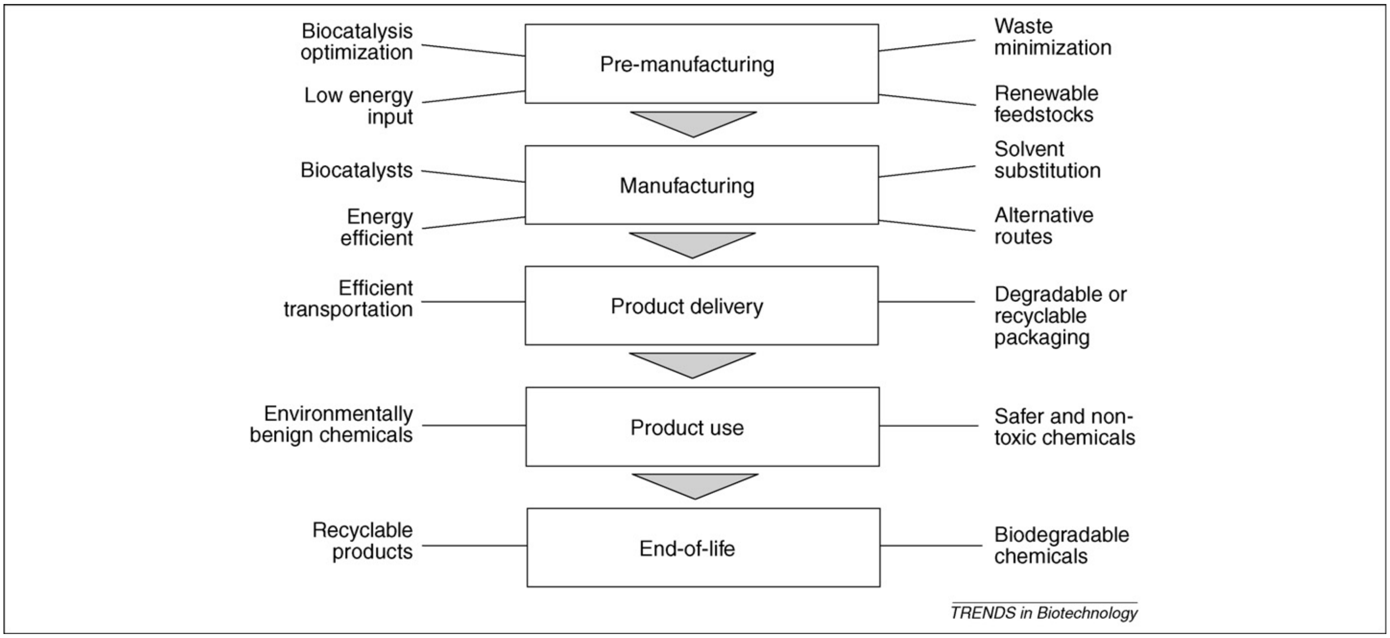

Figure 2. Green chemistry and industrial biotechnology applied from cradle-to-grave.

chemicals from renewable feedstock. Examples of a few bio-based products from a life cycle perspective are provided below.

Bioplastics from corn

A substantial fraction of the raw materials in the chemical industry is converted to polymers. Biodegradable polymers based on renewable raw materials have attracted considerable attention for replacing at least some of the traditional plastics [34]. Among these are polyhydroxyalkanoate (PHA) – a microbially synthesized polyester manufactured by Metabolix (http://www.metabolix.com) – and polylactic acid (PLA, NatureWorks™), a product of Cargill Dow (http://www.natureworksllc.com) from lactic acid generated by fermentation. The LCA for the production of PHA using corn as a feedstock showed no environmental benefits because the amount of fossil fuel used to produce 1 kg of PHA exceeds that required to produce an equal amount of the polystyrene it would replace [31].

The main hot spots in the life cycle of bioplastics with respect to energy input were the raw material production and the fermentation process, particularly in the case of PHA. Corn is one of the more energy-intensive crops and accounts for substantial amounts of fertilizer, insecticide and herbicide use. The subsequent transport and processing of the corn, involving wet milling and fractionation to yield gluten meal, oil, starch and sugar, also expend energy. For such a feedstock, the fuel source used for energy generation could have a profound impact on the environmental credentials of the product. If the overall energy demand was satisfied, for the large part, from non-fossil sources, products made from renewable resources could possess a substantially better energy balance compared with petrochemical polymers. Vink *et al.* have estimated that a substantial reduction in the gross fossil energy use and greenhouse-gas emissions can be achieved during PLA production if the lignin fraction of the biomass feedstock is used as a thermal energy source or, even better, by using wind power as the energy source [30]. The process also gains a substantial energy advantage if waste biomass is used as a feedstock [35]. Incineration or composting was suggested as a preferred option to landfill deposition for the waste management of the polymers made from renewable feedstocks [36].

Oleochemical products for wood coatings

Oleochemicals are hydrocarbons that are derived from vegetable oils; they are closely related to petrochemicals and are well suited for the transformations that are understood by the chemical industry. Microbial and enzymatic transformations can be used for the production of several oleochemical products [26]. As part of Greenchem, a research programme at Lund University in Sweden, biocatalytic and other 'green' processes are being evaluated for the production of coating, lubricant and surfactant products from oleochemicals (Figure 3). An assessment of the total energy consumption for wax ester production by lipase-catalysed esterification demonstrated that 34% less energy was consumed and less waste generated than by chemical esterification, where a strong acid is used as catalyst [37]. However, from a life-cycle perspective, comparison of the wax ester as a wood-coating ingredient with other coating products showed that UV-curable coatings based on fossil feedstock were the most favourable alternative in all environmental categories [38]. A similar observation was made using the eco-efficiency analysis method of BASF [28].

Most of the radiation-curable systems currently used are based on acrylates [39]. Epoxidized vegetable oils have found an application in cation-curable coatings prepared by exposure to UV radiation [40]. Oils with a high oxirane content (e.g. linseed oil) are preferred for coating applications, owing to the possibility of a high degree of epoxidation and, hence, extensive cross-linking [41]. A comparison of the LCAs for coatings based on acrylates

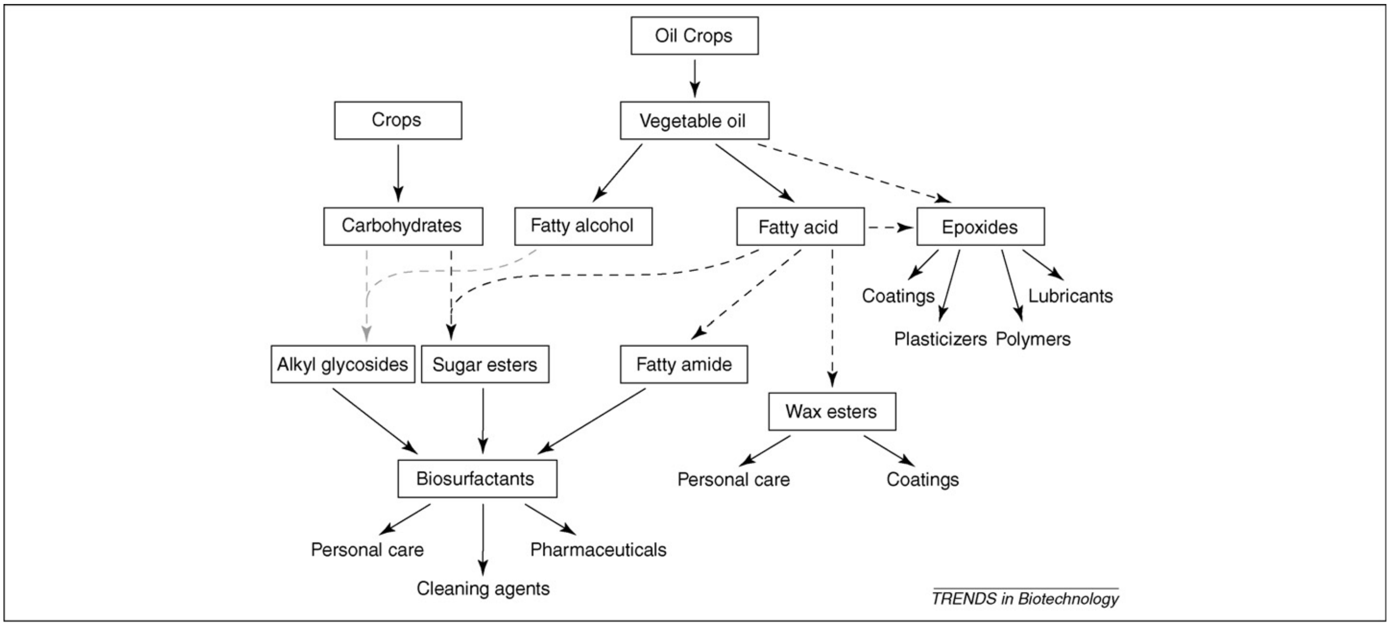

Figure 3. A glimpse of the potential of biocatalysis in transforming oleochemicals into various specialty chemicals. A vast amount of useful products in areas as diverse as personal care, pharmaceuticals, coatings, plasticizers and lubricants can be produced from bio-based raw materials using industrial biotechnology. Solid lines indicate the flow of main components from raw material to the end product; black broken lines refer to lipase-mediated reactions; and grey broken lines refer to reactions catalyzed by glycosidases used for producing the oleochemicals.

with those based on epoxidized vegetable oils showed an important ecological advantage for the latter [42].

There are potential alternative routes for the production of epoxidized oils or fatty acids. The industrial process used today involves the Prileshajev epoxidation reaction, in which a peracid is used for oxygen transfer to the double bonds in the fatty acid chains [43]. The peracid is usually formed *in situ* from hydrogen peroxide and acetic or formic acid, using a strong mineral acid or ion-exchange resin as catalyst. However, this process can also be performed in a milder and more selective way using a lipase as a catalyst [44]. This chemo–enzymatic process has also been performed under solvent-free conditions, adding further environmental benefits [45] and, in fact, addressing almost all of the above-mentioned principles of green chemistry. Furthermore, fewer coloured epoxidation products are obtained using the enzymatic route, which is indicative of the mild process conditions [46]. The major limitation of the process, however, is the low stability of the enzyme in the presence of the peroxide [47]. For an economical process, the lipase stability has to be improved, for example, by protein engineering. Another possibility would be to use a mono-oxygenase that can catalyse epoxidation directly from molecular oxygen and hence circumvent the use of hydrogen peroxide [48].

Yet another possibility for obtaining epoxidized oils is by direct extraction from plants. The oilseed crops *Euphorbia lagascae*, *Vernonia galamensis* and other *Vernonia* species possess vernolic acid, which has a natural epoxide content of 60–78% [46,49]. However, commercial production of these seed oils is hampered by high production costs due to low seed yield. Breeding programmes to develop more-productive plants has been attempted, with limited success so far. Genetic engineering to introduce the fatty acid biosynthetic machinery from the wild plants into a high-yielding oil crop has also been attempted, with low expression of the epoxidized product [50,51]. There remain considerable challenges before the promise of the ‘designer oil crops’ is translated into a large-scale commercial reality [52]. However, if successful, this approach would be attractive, from a LCA perspective, for the production of epoxidized and other oils with novel functionality.

Conclusion

The chemical industry is facing its second paradigm shift since the start of the petrochemistry industry: this time from petrochemistry to bio-based production. The main focus, so far, has been in developing the biofuel market, which is, in effect, driven by various policy incentives at different levels, for example, the carbon dioxide emission trading system induced by the Kyoto protocol, policy objectives concerning energy security, stimulation of renewable transportation fuels at an EU level, and the carbon dioxide tax on fossil fuels in Sweden. In the chemical industry, the use of fossil-based raw materials is often exempted from environmental taxes, leading to much weaker incentives for increasing the use of renewable feedstock. A crucial issue to be addressed would be the expansion of the existing policy instruments that favour the increased use of renewable carbon dioxide neutral feedstock in the chemical sector.

The biorefinery concept offers numerous possibilities to integrate the production of bio-energy and chemicals. This will also provide substantially higher value-added economic activities, besides promoting production in agriculture and forestry. Development of innovative and sustainable process technologies will be needed for realizing the shift to bio-based production of chemicals. The use of technologies that provide improved conversion efficiency – from raw material to final product – will increase the environmental benefits of bio-based products because the raw material production is the dominant step in the life cycle of the product. Industrial biotechnology is already making definite inroads into the chemical industry as an enabling technology, and its role will continue to grow during the coming years. So, too, will the use of environmental assessment tools in making the right choices of the available feedstocks and alternative technologies.

Acknowledgements
The financial support from the Swedish Foundation for Strategic Environmental Research (MISTRA) is gratefully acknowledged. The authors would like to thank Bo Mattiasson, Erik Andersson and Anna Petersson for their valuable help during the preparation of the manuscript.

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