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Utilisation of biomass for sustainable fuels and chemicals: Molecules, methods and metrics

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ABSTRACT

The various catalytic methodologies for the utilisation of renewable biomass for the sustainable production of liquid fuels and commodity chemicals are reviewed. Attention is focused on second generation processes starting from lignocellulose as a sustainable feedstock, thus circumventing the food vs fuel dilemma, and on the green features of these new processes. Emphasis is also placed on the need for establishing a set of metrics for assessing the sustainability of different processes and products. It is concluded that one set of metrics is probably not sufficient to assess the sustainability of both biofuels and platform commodity chemicals. The latter can probably be evaluated on the basis of E factors (kgs waste/kg product) that take both the carbon dioxide derived from energy consumption and water usage into account, perhaps together with some form of life cycle assessment. With biofuels on the other hand, the sheer magnitude of the volumes involved present extra issues, such as land usage, and the goal is different, i.e. to produce a particular energy density for an economically viable price in a sustainable fashion.

1. Introduction

One of the great challenges that society faces in the 21st century is the transition from an economy that is largely based on non-renewable fossil fuels as raw materials to one that is based on renewable resources and, according to the definition of sustainable development, meets the needs of the present generation without compromising the ability of future generations to meet their own needs [1]. Among various sustainable energy options (solar, wind, geothermal) only biomass, which encompasses agricultural food and feed crops, dedicated energy crops and trees, agriculture and forestry residues, aquatic plants, and animal and municipal wastes, is a source of carbon-based fuels and chemicals.

The switch from non-renewable fossil fuels to renewable biomass as a feedstock for liquid fuels and commodity chemicals will afford various economic, environmental and social benefits: (i) a more stable and secure supply of feedstocks, (ii) an environmentally beneficial reduction in the carbon footprint of chemicals and liquid fuels, and (iii) a more stable and profitable agricultural economy. Interestingly, these three major drivers of the bio-based economy constitute the three pillars of sustainability: profitability, planet and people. An additional benefit will be that many existing products will be substituted by alternatives that are inherently safer and have a reduced environmental footprint, for example, biocompatible and biodegradable polymers.

First generation biofuels (bioethanol and biodiesel) and bio-based commodity chemicals such as lactic acid and 1,3-propane diol are currently being produced from starch, sucrose and vegetable oils as feedstocks. However, the availability of the latter is limited by the amount of fertile soil and the yield per hectare and they compete, directly or indirectly, with food production, which is already effecting the price of food. It is abundantly clear, therefore, that this is not a sustainable solution for the long term. In contrast, it is widely acknowledged that the next generation of bio-based fuels and platform chemicals will utilise lignocellulosic biomass and inedible oilseed crops as feedstocks in integrated biorefineries [2,3].

In order to be sustainable, biomass utilisation will depend heavily on the successful deployment of innovative, green chemistry, defined as [4,5].

Green chemistry efficiently utilises (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.

Waste minimisation will inevitably involve the application of green catalytic methodologies (homogeneous, heterogeneous and enzymatic) [3,6].

2. Metrics of green chemistry: the E factor and atom economy

How will we know if a process for the conversion of biomass to fuels and/or chemicals is sustainable or not? As Lord Kelvin once

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Table 1
The E factor.

Industry segment	Volume (tons/annum)[a]	E factor (kg waste/kg product)
Bulk chemicals	10^4–10^6	<1 to 5
Fine chemical industry	10^2–10^4	5 to >50
Pharmaceutical industry	10–10^3	25 to >100

[a] Annual production of the product world-wide or at a single site.

remarked, "*To measure is to know*". Indeed, attention was drawn to the problem of waste generation in the chemical industry by the introduction, in 1992, of the E(nvironmental) factor (kgs waste/kg product) as a metric for quickly assessing the environmental footprint of manufacturing processes [7–10]. Table 1 illustrates the magnitude of the waste problem in the various segments of the chemical industry.

The E factor is the *actual amount* of waste produced in the process, defined as everything but the desired product. It takes the chemical yield into account and includes reagents, solvent losses, process aids and, in principle, even energy consumption. A higher E factor means more waste and, consequently, a larger environmental footprint. The ideal E factor is zero. Put quite simply, it is kilograms (of raw materials) in, minus kilograms of desired product, divided by kilograms of product out. It can be easily calculated from a knowledge of the number of tons of raw materials purchased and the number of tons of product sold, for a particular product or a production site or even a whole company. Quantification of the waste generated in chemicals manufacturing, by way of E factors, served to focus the attention of fine chemical and pharmaceutical companies on the need for a paradigm shift from a concept of process efficiency which was exclusively based on chemical yield to one that is motivated by elimination of waste and maximisation of raw materials utilisation. Indeed, over the last two decades the E factor has been widely adopted by the fine chemicals and pharmaceutical industries [11–13].

Another popular green metric is what we originally called *atom utilisation* [14] but what has become more widely known as *atom economy* following the seminal publications of Trost [15,16]. Atom economy (AE) is a theoretical number that can be derived from a knowledge of the stoichiometric equation of the reaction(s) involved. It assumes a chemical yield of 100% of theoretical and that reactants are used in exactly stoichiometric amounts. It disregards substances, such as solvent and acids or bases used in work-up, which do not appear in the stoichiometric equation. Hence, it is an excellent method for quickly providing a rough estimate of the amount of waste that will be generated by different processes before any experiments are performed. It is complementary with respect to the E factor which provides data on the actual amounts of waste formed based on experimental data.

A limitation of the E factor is that it takes only the mass of waste generated into account. However, the environmental footprint of waste is determined not only by its amount but also by its nature. Hence, we introduced [8] the term 'environmental quotient', EQ, obtained by multiplying the E factor with an arbitrarily assigned unfriendliness quotient, *Q*. For example, one could arbitrarily assign a *Q* value of 1 to NaCl and, say, 100–1000 to a heavy metal salt, such as chromium, depending on its toxicity, ease of recycling. Although the magnitude of *Q* is debatable and difficult to quantify, 'quantitative assessment' of the environmental impact of waste is, in principle, possible. *Q* is dependent on, *inter alia*, the ease of disposal or recycling of waste and, generally speaking, organic waste is more easy to dispose of or recycle than inorganic waste.

3. The role of catalysis and alternative reaction media

A major source of waste is inorganic salts such as sodium chloride, sodium sulfate, and ammonium sulfate that are formed in the reaction or in downstream processing. One of the reasons that the E factor increases dramatically on going from bulk to fine chemicals and pharmaceuticals is that the latter are more complicated molecules that involve multi-step syntheses. However, the larger E factors in the fine chemical and pharmaceutical industries are also a consequence of the widespread use of classical stoichiometric reagents rather than catalysts. Examples which readily come to mind are classical stoichiometric metal oxidants such as permanganate, manganese dioxide and chromium(VI) reagents and metal hydride ($LiAlH_4$, $NaBH_4$) reducing agents. Similarly, a multitude of classical organic reactions, such as sulfonations, nitrations, halogenations, diazotisations and Friedel–Crafts acylations, employ stoichiometric amounts of mineral acids (H_2SO_4, HF, H_3PO_4) or Lewis acids ($AlCl_3$, $ZnCl_2$, BF_3) and are major sources of inorganic waste. Another major source of waste in the fine chemical and pharmaceutical industries is solvent losses that end up as emissions to the atmosphere or in aqueous effluent. Indeed, the use of many traditional organic solvents, such as chlorinated hydrocarbons, has been severely curtailed and the whole question of solvent use has become a major issue in the manufacture of pharmaceuticals [17]. The problem with solvents is not so much their use but the seemingly inherent inefficiencies associated with their containment, recovery and reuse. In our original studies of E factors we assumed, if details were not known, that solvents would be recycled by distillation and that this would involve a 10% loss.

Having established the major causes of waste, the solution to the waste problem is evident: the widespread substitution of classical syntheses employing stoichiometric amounts of inorganic (or organic) reagents by cleaner, catalytic alternatives [3] and the use of alternative reaction media [18,19]. The best solvent is no solvent but if a solvent is needed there should be provisions for its efficient removal from the product and reuse. The use of water and supercritical carbon dioxide as alternative reaction media are interesting in the context of biomass conversion as they are formed as byproducts and the feedstock is ultimately derived from these raw materials and in many cases is dissolved in water. We also note, in this context, that there is considerable interest in the use of ionic liquids as reaction media for biomass conversion processes [20] (see later).

We generally excluded water from the calculation of the E factor as we thought that its inclusion would lead to exceptionally high E factors in many cases and make meaningful comparisons of processes difficult. For example, when considering an aqueous waste stream we counted only the inorganic salts and organic compounds contained in the water and excluded the water itself. However, there is a definite trend in the pharmaceutical industry towards the inclusion of water in the E factor and water usage is likely to become a crucial issue in comparing processes for biomass conversion (see later).

4. Life cycle assessment and sustainability

Another approach to assessing the environmental impact and, hence, sustainability of both products and processes in general is life cycle assessment (LCA) [21,22]. This involves the evaluation of products and processes within defined domains, e.g. cradle-to-gate, cradle-to-grave and gate-to-gate, on the basis of quantifiable environmental impact indicators, such as energy usage, greenhouse gas emissions, ozone depletion, acidification, eutrophication, smog formation, and ecotoxicity, in addition to waste generated. LCA is clearly complementary with respect to E factors (see later for an example).

5. Meaningful metrics for biomass utilisation

Since E factors and atom economy (AE) have been widely used for assessing the environmental footprint of chemical manufacturing processes they would appear to be a good starting point for evaluating processes for biomass utilisation. However, evaluation of competing processes is fraught with various complicating factors inherent to biomass utilisation, many of which are a consequence of the enormous scale that is envisaged. The continuing, unresolved 'net energy debate' illustrates the difficulty involved in reaching a consensus on meaningful metrics for biofuels. Leading scientists cannot agree on how to calculate 'net energy' and, hence, whether or not biofuels such as bioethanol have a positive net energy [23]. There is a clear need for conceptual clarity in this area.

Some of the issues to be addressed are:

- Mass vs energy balance in biobased fuels and chemicals production.
- Where to start with calculating E factors in the cradle-gate-gate-grave-cradle cycle?
- What are the E factors of fermentation processes?
- What is Q for biomass utilization processes?
- The food vs fuel dilemma.
- Land and water usage.

Bearing in mind the goals of biomass utilisation as outlined in the Introduction the sustainability of biofuels could be assessed on the basis of their potential to replace crude oil (feedstock security goal), on greenhouse gas reductions per km driven (environmental goal) and on efficiency of land usage [24]. On the other hand, biobased chemicals manufacture accounts for less than 10% of the crude oil that is converted to liquid biofuels, which means that, for example, the food vs fuel dilemma and land usage are generally not serious issues with the former. In other words, the weighting of the various factors in the green metrics should be different for biofuels and biobased chemicals. We note, however, that biobased chemicals may be indirectly influenced if they are produced with biofuels in an integrated biorefinery. Indeed, because of the enormous scale of liquid fuels production, it is likely that the production of chemicals from biomass will be driven by the production of liquid fuels.

5.1. Primary processes of biomass conversion

As noted above, it is generally accepted that the second generation of biofuels will be derived from lignocellulosic feedstocks. Lignocellulose is the fibrous material that constitutes the cell walls of plants and is much more difficult to convert than the first generation renewable feedstocks – sugars, starches and vegetable oils – but its use will dispense with the food vs fuel debate associated with the latter feedstocks [25]. It consists of three major polymeric components: lignin (ca. 20%), cellulose (ca. 40%), and hemicellulose (ca. 25%). Irrespective of whether the final destination is biofuels or biobased commodity chemicals, the first hurdle to be overcome is the primary conversion of the lignocellulose feedstock. It has to be depolymerised and (partially) deoxygenated in order to convert it to fuels and chemicals.

There are basically two methods for this primary conversion: thermochemical and hydrolytic (see Fig. 1) [26]. The former involves pyrolysis to a mixture of charcoal and pyrolysis oil or gasification to afford syn gas (a mixture of carbon monoxide and hydrogen), analogous to syn gas from coal gasification [27]. The syn gas can be converted to liquid fuels or chemicals *via* existing technologies such as the Fischer–Tropsch process or methanol synthesis, respectively [27]. Alternatively, lignocellulose can be hydrolysed, in the presence of mineral acids at elevated temperatures or enzyme cocktails under milder conditions, to afford a mixture of lignin, hemicellulose and cellulose. In the former case copious amounts of inorganic salt, e.g. sulfates, are formed, as a result of neutralisation of the dilute mineral acid used, leading to high E factors. Consequently, attention is being focused on the design of solid acid catalysts for the conversion of biomass [28,29] by analogy with the processing of crude oil fractions in the petrochemical industry. In the case of enzymatic hydrolysis some form of pretreatment, such as a steam explosion, is generally necessary to open up the lignocellulose structure and render the targeted ether and ester bonds accessible to the enzymes [30]. The lignin can be used to generate electricity and the cellulose and hemicellulose can be further hydrolysed to mixtures of glucose and pentose sugars, respectively. It is also worth noting, in the context of bioconversion that many organisms are equipped with the necessary biochemical machinery to selectively break down lignocellulose. The termite, for example, is very adept at it and the enzymes involved in the termite digestome would seem worthy of further study [31]. It has also been suggested [32] that reverse bio-engineering of lignocellulose biosynthesis could provide a fruitful approach to the selective degradation of cellulose.

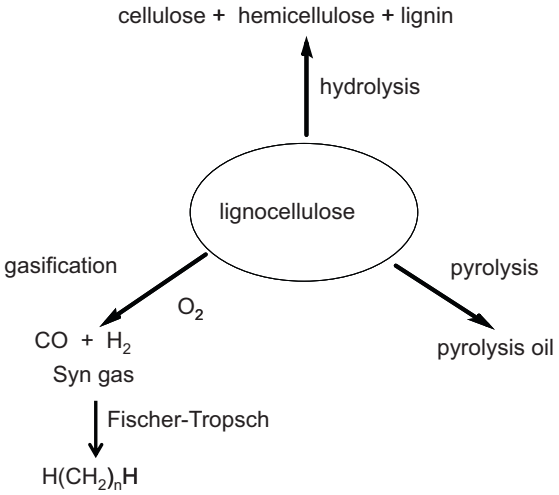

Fig. 1. Primary conversion of lignocellulose.

Generally speaking, the reaction medium for primary conversion of lignocelluloses will be water but alternative reaction media, in particular ionic liquids [33] are the focus of considerable attention in this context. Zhao and coworkers [34] reported the direct conversion of lignocelluloses feedstocks, such as corn stalk, rice straw, pine wood and bagasse, to a mixture of monosaccharides (mainly glucose and xylose) in 66–81% yield by heating with HCl at 100 °C for 30–60 min in the ionic liquid, 1-butyl-3-methylimidazolium chloride, $[bmim]^+$ $[Cl]^-$. This is a promising development but, in order to become economically and environmentally viable, the dialkyl imidazolium ionic liquid needs to be replaced by a less expensive, non-toxic and biodegradable ionic liquid, preferably produced from a renewable raw material [35].

Secondary conversion of the sugars to commodity platform chemicals, can be achieved through abiological or biological processes. For example, they can be converted by hydrolysis to furfural, hydroxymethylfurfural and levulinic acid which can be further converted to a variety of chemicals (see later). Alternatively, the sugars can be fermented to bioethanol or biobutanol or to other commodity chemicals such as lactic acid or 1,3-propane diol.

As noted above, first generation biodiesel is probably not sustainable in the longer term as it is derived from edible plant or seed oils. Second generation biodiesel could be produced from

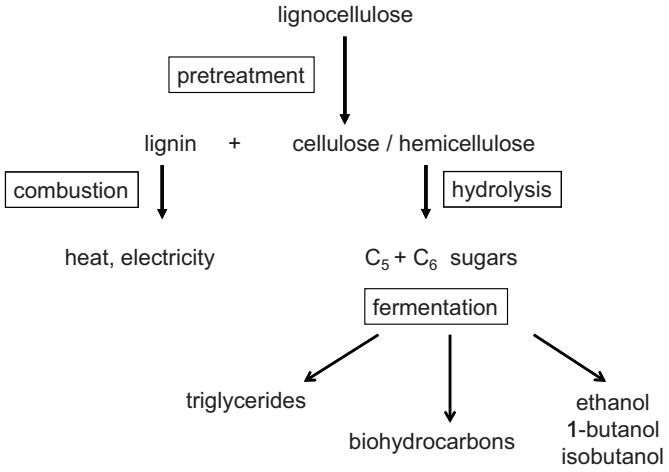

Fig. 2. Different approaches to 2nd generation biofuels from lignocellulose.

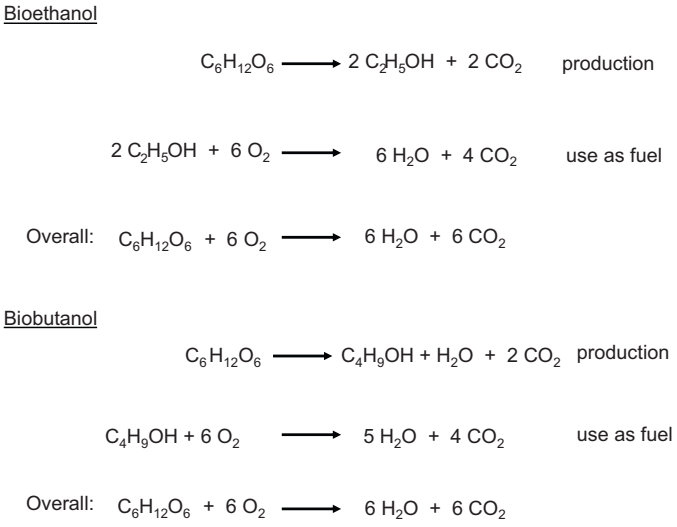

Fig. 4. Atom economy of bioethanol vs biobutanol.

inedible plant oils or waste oils. Alternatively, the triglyceride feedstock could be produced from (lingo)cellulose by fermentation with oleaginous yeasts [36]. However, the feasibility of sustainable biodiesel production from microalgae has been questioned [37]. Yet another alternative for the longer term is to use metabolic engineering to produce diesel range hydrocarbons directly from cellulose by bacterial or yeast fermentation or directly from engineered photosynthetic algae [38]. The different options starting from hydrolysis of lignocellulose are summarized in Fig. 2.

5.2. Atom economy of biomass conversion to liquid fuels

In Fig. 3 we compare the atom economies of four different processes for the conversion of glucose to liquid fuels: fermentation to ethanol or butanol or *via* pyrolysis or gasification and subsequent Fischer–Tropsch synthesis.

However, it is important to emphasize that we are not comparing different processes to the same product but rather processes to different products with the same application, i.e. a liquid transportation fuel. What we are ultimately interested in is a comparison on the basis of how many kilometers per liter product an automobile can travel as a result of the combustion of this product, i.e. its energy density, divided by its price per liter? As shown in Fig. 4, if we make a comparison on the basis of both production and combustion of the products then the overall atom economy for bioethanol and biobutanol is the same.

In contrast, in the drive towards biobased manufacture of commodity chemicals we are generally concerned with the comparison of existing processes based on petrochemical feedstocks with new processes based on renewable biomass *to the same product*. Hence, we conclude that the same set of metrics are unlikely to be suitable for assessing the sustainability and/or greenness of both chemicals and fuels from biomass. Furthermore, it may be necessary to consider the metrics associated with the feedstock up to its delivery to the gate and the metrics of its conversion to products, be it biofuels or chemicals, separately. Girio and coworkers [39] have, for example, proposed a biotechnological valorization potential indicator for assessing the suitability of lignocellulosic materials as feedstocks in a biorefinery.

5.3. Green metrics of biotransformations

Biocatalysis has many benefits to offer in the context of green chemistry and sustainability. Reactions are performed under mild conditions (physiological pH and ambient temperature and pressure) in an environmentally compatible solvent (water) using a

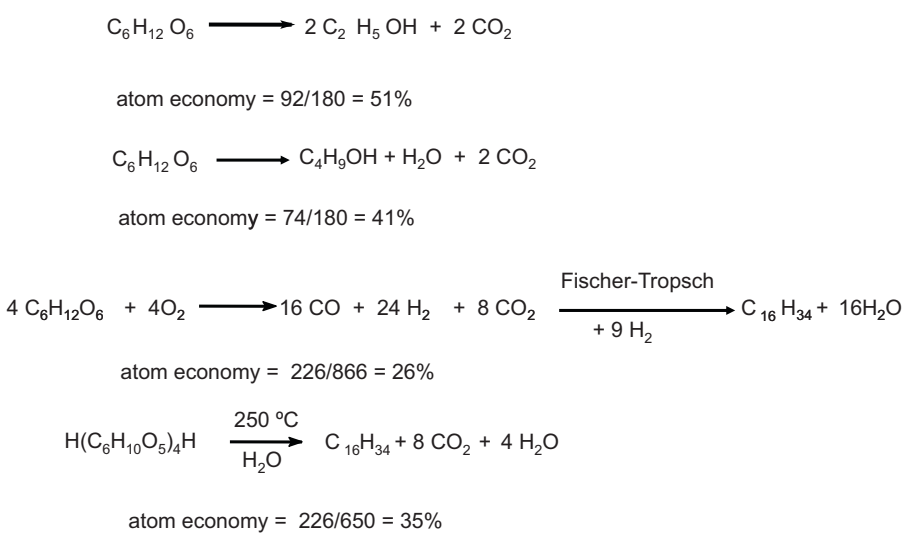

Fig. 3. Atom economies of various processes for glucose to liquid fuel conversions.

biodegradable catalyst (an enzyme) that is itself derived from renewable resources. This affords processes which are less energy intensive, generate less waste and are both environmentally and economically more attractive than conventional routes. As a direct consequence of the higher selectivities and milder reaction conditions, they often afford products in higher quality than traditional chemical or chemo-catalytic processes.

Biotransformations can be performed with isolated enzymes or as whole cell processes. The former have the advantage of not being contaminated with other enzymes present in the cell while the latter is less expensive as it avoids separation and purification of the enzyme. In the case of dead cells, the E factors of the two methods are essentially the same; the waste cell debris is separated before or after the biotransformation. In contrast, when growing microbial cells are used i.e. in fermentation processes, substantial amounts of waste biomass can be generated. However, this is generally easy to dispose of, e.g. as animal feed or can, in principle, be used as a source of energy for the process. On the other hand, many fermentation processes involve, as a result of pH changes, the formation of copious quantities of inorganic salts that may be the major contributor to waste.

To our knowledge no E factors of fermentation processes have been reported. The mass balances of a few fermentation processes have been documented by Petrides [40] from which E factors can be calculated. For example, the E factor for the bulk fermentation product, citric acid, is 1.4 which compares well with the E factor range of <1–5 typical of bulk petrochemicals (see Table 1). Roughly 75% of this waste consists of calcium sulfate. During the process calcium hydroxide is added to control the pH, affording calcium citrate which is reacted with sulfuric acid to produce citric acid and calcium sulfate. Inclusion of water in the calculation afforded an E factor of 17.

It was recently reported [28] that the E factor of cellulosic ethanol is a staggering 42. However, if water (36.8 kg/kg ethanol) and carbon dioxide (4.1 kg/kg ethanol) are excluded, the E factor drops to a more reasonable 1.1. It was further noted that a cellulosic ethanol plant processing 10,000 tons of lignocellulose feedstock per day would produce 870 tons of ethanol and generate 32 million liters of wastewater daily, i.e. enough water to supply a town of 300,000 inhabitants. Moreover, this water is contaminated with organic byproducts, thus necessitating a sophisticated industrial waste water treatment in order to decrease their concentrations to the ppm level or below and enable reuse of the water.

Fermentation processes for the production of therapeutic proteins (biopharmaceuticals) can have very high E factors, even compared with those observed for small molecule drugs. The production of recombinant human insulin [40], for example, involves an E factor of ca. 6600. The most important contributors to the waste are urea, acetic acid, formic acid, phosphoric acid, guanidine hydrochloride, glucose, sodium chloride, sodium hydroxide and acetonitrile. If water is included the E factor becomes a staggering 50,000.

Biotransformations involving the use of isolated enzymes, in contrast, tend to involve significantly higher substrate concentrations and combine a higher productivity with a lower water usage compared to fermentations. For example, the Codexis, green-by-design, three-enzyme process (Fig. 5) for the synthesis of a key intermediate for atorvastatin, the active ingredient of the cholesterol lowering drug Lipitor®, has an E factor of 5.8 [41,42] if water is excluded. If process water is included the E factor for the whole process is 18. The main contributors to the E factor are sodium gluconate (25%), NaCl and Na_2SO_4 (combined ca. 22%) and solvent (EtOAc and BuOAc) losses (51%). The three enzymes and the NADP cofactor account for <1% of the waste. The main waste streams are aqueous and directly biodegradable.

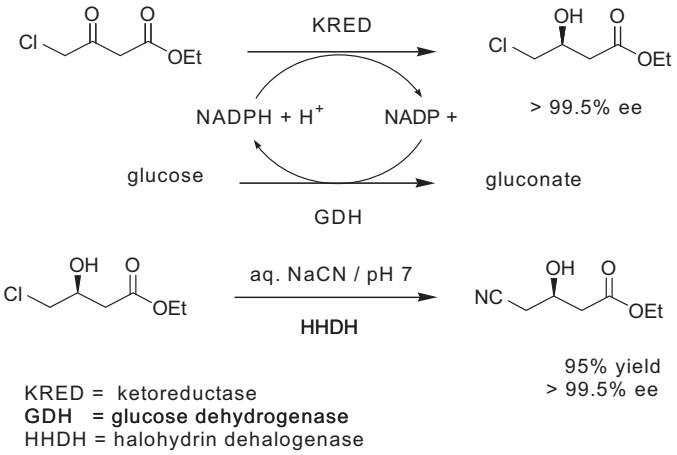

Fig. 5. Codexis process for atorvastatin intermediate.

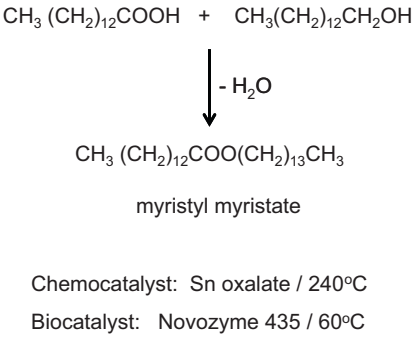

Fig. 6. Chemo- vs biocatalytic production of myristyl myristate.

Biotransformations are also being widely applied in the cosmetics ingredients industry, even with relatively simple products such as emollients based on fatty acid esters. For example, a recent report [43] compared the industrial scale synthesis of the emollient ester, myristyl myristate, by chemocatalytic vs enzymatic esterification (Fig. 6). The former involved the use of tin(II) oxalate as a catalyst at 240 °C for 4 h and the latter employed an immobilized form of *Candida antarctica* lipase B, Novozyme 435, at 60 °C for 12 h.

The atom economy and the E factor of both processes is 96% and <0.1, respectively, even when waste water is included. Consequently, the environmental impacts of the two processes were evaluated in a cradle-to-gate environmental life cycle assessment (LCA) on the basis of five impact categories: (i) energy consumption, (ii) global warming (greenhouse gas emissions), (iii) acidification, (iv) nutrient enrichment and (v) smog formation (volatile organics). As shown in Table 2 substantial reductions in all categories were achieved. Energy consumption was reduced by more than 60% and the formation of undesirable pollutants by up to 90%. Replacement of an environmentally unattractive tin catalyst by an enzyme and the considerably milder conditions were the major

Table 2
Key environmental parameters of chemo- vs biocatalytic esterification.

Parameter	Units	Chemocatalytic	Biocatalytic	Savings
Energy	GJ	22.5	8.63	62%
GHG emissions[a]	kg CO_2 eq.	1518	582	62%
Acidification[b]	kg SO_2 eq.	10.58	1.31	88%
Eutrophication	kg PO_4 eq.	0.86	0.24	74%
VOC emissions	kg C_2H_4 eq.	0.49	0.12	76%

[a] Greenhouse gas emissions.
[b] Volatile organics (smog formation).

Table 3
Biobased platform chemicals from renewable carbohydrate feedstocks.

DOE report 2004	Bozell and Petersen [44]
Fumaric acid	Ethanol
Malic acid	Lactic acid
Succinic acid	Succinic acid
3-Hydroxypropionic acid	3-Hydroxypropionic acid
Aspartic acid	Isoprene
Glucaric acid	Biohydrocarbons
Aspartic acid	Furfural
Glutamic acid	Hydroxymethylfurfural
2,5-Furan dicarboxylic acid	2,5-Furan dicarboxylic acid
Levulinic acid	Levulinic acid
Sorbitol	Sorbitol
Xylitol/arabinitol	Xylitol
Glycerol/derivatives	Glycerol/derivatives
Itaconic acid	
3-Hydroxybutyrolactone	

factors responsible for the significantly more eco-friendly profile of the biocatalytic process.

In addition to the above mentioned benefits, the product quality was much higher in the biocatalytic process, mainly as a result of the much milder reaction conditions. This meant that purification steps could be largely circumvented, resulting in simpler downstream processing. Thus, better product quality and process simplification are added economic benefits of the biocatalytic vs the chemocatalytic process.

6. Bulk chemicals from biomass

Biorefinery development in the USA has two strategic goals: the replacement of imported crude oil in favor of renewable domestic raw materials (an energy goal) and the establishment of a robust biobased industry (an economic goal) [44]. The integration of biofuels and biobased commodity chemicals manufacture in a biorefinery offers a much higher return on investment than with biofuels alone and meets the energy and economic goals simultaneously. However, biobased chemical production is challenged by a lack of conversion technologies and a plethora of target molecules. Integrated biorefineries are still in their infancy and a core group of basic chemicals, with appropriate technologies to make them, still has to be identified. In 2004 the US Department of Energy (DOE) published a report describing a group of 15 target molecules that could be produced from renewable carbohydrate raw materials [45]. In the ensuing six years considerable progress has been made in the development of technologies for biobased chemicals production and Bozell and Petersen [44] have recently updated the list and arrived at a list of thirteen target products. The two lists are compared in Table 3.

Examples of first generation commodity chemicals currently being produced from corn starch are (*S*)-lactic acid and 1,3 propane diol (Fig. 7). However, it is envisaged that in the not too distant future biorefineries will utilise lignocellulosic feedstocks to produce a range of platform chemicals, such as succinic, acrylic and methacrylic acids and caprolactam (Fig. 7).

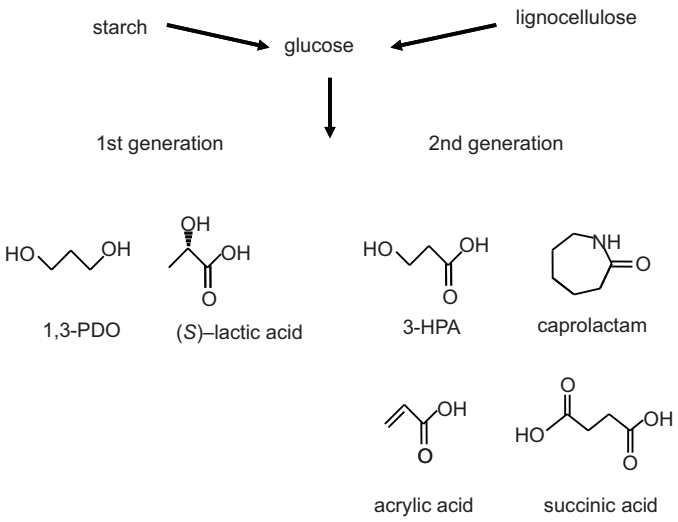

Fig. 7. Biobased platform chemicals: today and tomorrow.

Ethanol and lower alcohols (propanol and butanols) are of interest as precursors to the corresponding olefins, thereby providing a direct link between biorefinery technologies and the existing petrochemicals industry. If ethylene and 1-butene were available, from ethanol and 1-butanol, respectively, then propylene could be made by olefin metathesis, thus completing the C2, C3 and C4 triad that forms the basis of the petrochemical industry. Interestingly, Dow and Solvay have already announced plans to build ethanol-to-ethylene plants based on a first generation renewable feedstock (sugar cane). Indeed, it has been suggested that the optimum use of bioethanol could well be as a platform chemical [46]. In this context it is interesting to consider the technology recently developed by Zeachem [47] for the acetogenic fermentation of glucose to acetic acid. In contrast to the fermentative production of ethanol, which generates one molecule of carbon dioxide for every molecule of ethanol, acetogenic fermentation is 100% atom efficient, affording three molecules of acetic acid per molecule of glucose (Fig. 8). In the Zeachem process the acetic acid is subsequently esterified with ethanol, to produce ethyl acetate, which is hydrogenated to produce overall three molecules of ethanol from one molecule of glucose.

Hence, the Zeachem process is able to produce three commodity chemicals – acetic acid, ethyl acetate and ethanol – by a combination of fermentation and a chemocatalytic conversion. The ethanol can be marketed as a biofuel and or commodity chemical. The hydrogen necessary for the hydrogenation step is generated by gasification of the lignin produced from the envisaged lignocellulosic feedstock. In order to compare the E factor of the Zeachem process with that of the conventional production of ethanol by fer-

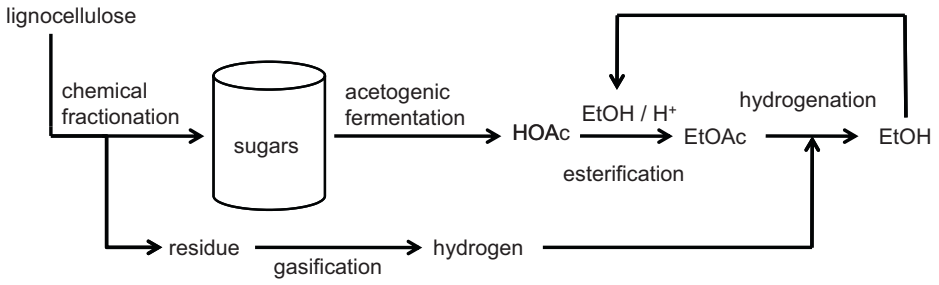

Fig. 8. Zeachem process for acetic acid and ethanol *via* acetogenic fermentation.

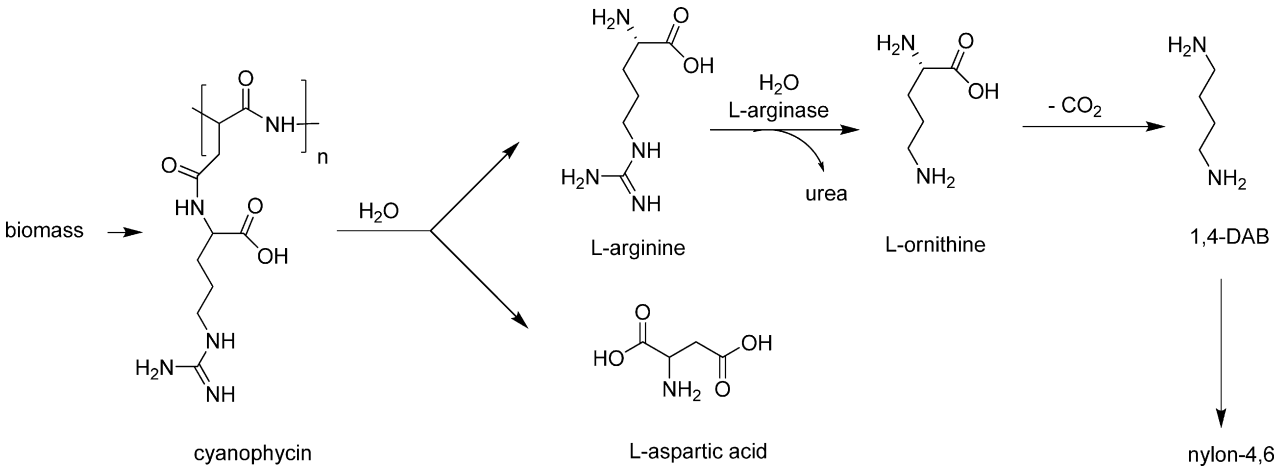

Fig. 9. Conversion of cyanophycin (CGP) to 1,4-diaminobutane.

mentation the carbon dioxide formation as a result of the energy consumed in the generation of the hydrogen and in the hydrogenation step needs to be compared with the carbon dioxide formed in the conventional ethanol fermentation. Hence, E factors incorporating both carbon dioxide formed directly in the reaction and from energy consumption should provide a meaningful comparison of the two processes.

Currently much attention is being focused on the production of other lower alcohol biofuels by fermentation of carbohydrates derived from biomass. For example, 1-butanol [48] is being developed in a DuPont/BP cooperation and the company Gevo is commercializing technology developed by Liao and co-workers for the production of isobutanol by an engineered *Escherichia coli* strain [49]. As already mentioned above, these alcohols could, *via* dehydration to 1-butene and isobutene, provide another link into existing petrochemical supply chains.

The direct fermentative production of hydrocarbons is also a focus of much recent attention within the biofuels arena. Metabolic engineering is being used to re-engineer the isoprenoid pathway or fatty acid biosynthesis, in bacteria or yeast, to directly yield hydrocarbons. Here again the envisaged products can be marketed as biofuels and/or biobased commodity chemicals. A pertinent example is the production of the sesquiterpene, farnesene, in a genetically modified yeast being developed by the company Amyris [50]. Another California company, LS9, is pursuing the re-engineering of the fatty acid synthesis pathway in bacteria to produce long chain hydrocarbons [49]. Alternatively, the fungus, *Gliocladium roseum*, has been shown to convert cellulose into a mixture of diesel range hydrocarbons [51]. Similarly, algae can also be engineered to excrete hydrocarbons, an avenue being pursued by a partnership between Exxon Mobil and Synthetic Genomics [52].

Economically viable production of a variety of commodity organic acids by fermentation is envisaged and included in the list in Table 3. Lactic acid is an example of a first generation biobased commodity chemical. Examples of second generation products are: succinic acid [38,53] and 3-hydroxypropionic acid (as a precursor to acrylic acid).

The sugar alcohols, xylitol and sorbitol, produced by hydrogenation of xylose and glucose, respectively, and glycerol, the byproduct of biodiesel manufacture, complete the list. The latter has the potential to become an important platform chemical in a biorefinery, assuming that biodiesel will consist of fatty acid esters and be produced by transesterification of triglycerides in the long term.

The dehydration of pentoses and hexoses, derived from hemicellulose and cellulose, affords furfural and hydroxymethyl furfural (HMF), respectively. The latter can be further converted to levulinic acid and valerolactone or to furan-2,5-dicarboxylic acid, a potential building block for polyesters (see later).

7. Amino acids as biobased platform chemicals

Biomass is derived from living matter, e.g. plants, and as such contains a small amount of protein which could be separated prior to processing. Because of the enormous volumes of biomass required for the manufacture of biofuels in a biorefinery this small amount could be of the order of millions of tons on an annual basis. Consequently, the constituent amino acids of this protein side-stream could become interesting platform chemicals [54], assuming that methods could be developed to separate individual amino acids or selectively convert them *in situ*. For example, it has been suggested that nitrogen-containing commodity chemicals could be more economically made, and with a smaller environmental footprint, from such biomass-derived amino acids than from petroleum hydrocarbons [55].

Interestingly, the list of chemicals in the 2004 DOE report contained two amino acids: glutamic and aspartic acids. In their recent update, Bozell and Petersen [44] omitted these two products from the list on the basis that they have remained essentially terminal products of the chemical industry. However, on the basis of the foregoing discussion we believe that there is due cause to reinstate certain natural amino acids as future platform chemicals. For example, L-lysine can be converted to caprolactam, the precursor of Nylon 6, and L-phenylalanine can afford styrene, *via* deamination to cinnamic acid and subsequent decarboxylation [55]. In a similar vein, it was recently proposed [56] that cyanophycin (CGP), a polypeptide produced *in vivo* by cyanobacteria as a nitrogen storage polymer, is a potential source of nitrogen containing commodity chemicals. CGP consists of a poly(L-aspartic acid) backbone with equimolar amounts of L-arginine side chains. Heterologous expression in industrially relevant bacterial hosts provides the possibility for the economically viable production of CGP and recent work on *Saccharomyces cerevisiae* suggests that co-production of CGP and ethanol from agricultural wastes could be feasible. Since it is insoluble under physiological conditions, CGP can be easily isolated. It was suggested that the arginine could be converted to the industrial monomer, 1,4-diaminobutane, *via* L-arginase catalyzed hydrolysis to L-ornithine and subsequent decarboxylase catalyzed decarboxylation (Fig. 9).

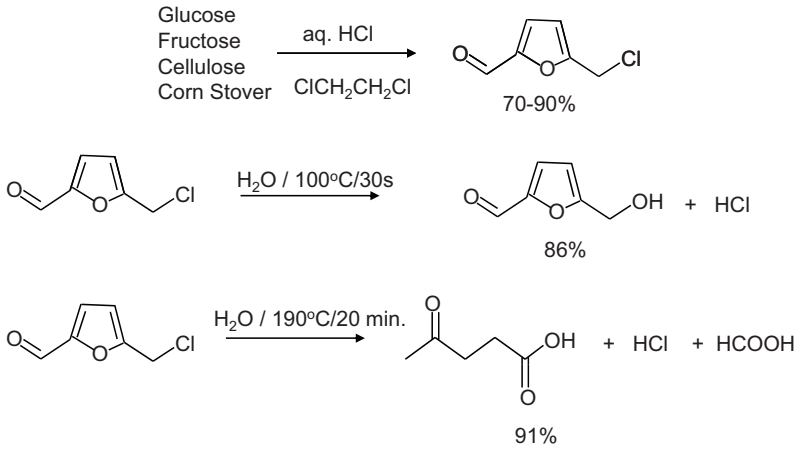

Fig. 10. Chemical conversion of carbohydrates to HMF or levulinic acid (LA).

8. Advances in chemocatalytic conversion of carbohydrates

Dehydration of pentoses and hexoses to furfural and hydroxymethyl furfural (HMF), respectively, traditionally proceeded in relatively low selectivities. However, recent developments suggest that these dehydrations can be performed much more selectively with metal chloride catalysts in ionic liquids as reaction media [57]. Further reaction of HMF with water, under acidic conditions, affords levulinic acid with elimination of formic acid. Alternatively, it was recently shown [58] that glucose, fructose, cellulose or even corn stover could be directly converted to chloromethyl furfural (CMF) in high yield by reaction with aqueous HCl at 100 °C. Subsequent reaction of the CMF with water afforded, depending on the temperature, high yields of HMF or levulinic acid (LA), with concomitant regeneration of the HCl (see Fig. 10). Unfortunately, the reaction was conducted in 1,2-dichloroethane but presumably this could be replaced by a more environmentally acceptable solvent.

HMF can be converted in high yield to the dimethyl ester of furan-2,5-dicarboxylic acid (FDCA) by catalytic aerobic oxidation over a nanogold-on-titania catalyst [59]. Alternatively, we showed [60] that homogeneous palladium catalyzed carbonylation of HMF, in water as the reaction medium, afforded carboxymethylfurfural in high yield (Fig. 11).

Poliakoff and coworkers [61] showed that hydrogenation of aqueous LA over a ruthenium catalyst, in supercritical carbon dioxide as reaction medium, affords γ-valerolactone (GVL) in 100% selectivity (Fig. 12). The LA partitions into the aqueous phase and the GVL into the carbon dioxide phase. Alternatively, the hydrogen could be replaced by the formic acid generated as a byproduct

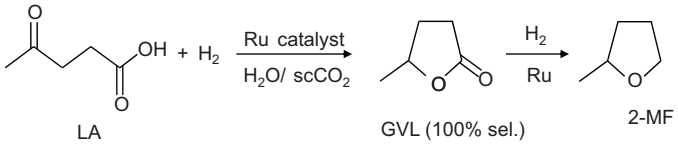

Fig. 12. Hydrogenation of levulinic acid to γ-valerolactone.

in the formation of LA from HMF [62]. Horvath has proposed GVL as an ideal sustainable liquid fuel and platform chemical [62,63]. For example, ring opening with methanol, followed by dehydration, affords methyl pentenoate, a potential precursor of dimethyl adipate and, hence, a nylon-6,6 intermediate [64].

An alternative to utilising HMF, LA and GVL as platform chemicals is to convert them to hydrocarbon fuels by processes involving combinations of acid catalyzed dehydration and catalytic hydrogenation. The hydrogen required can be produced by catalytic aqueous reforming of the carbohydrate feedstock [65]. Alternatively, it has been suggested that HMF could be converted to 5-ethoxymethylfurfuryl alcohol by etherification with ethanol and subsequent hydrogenation, thus providing a potential diesel fuel additive from two renewable feedstocks and hydrogen [66].

Another interesting development in the area of chemocatalytic conversion of carbohydrates is the recently reported [67] one-pot conversion of cellulose into isosorbide using a hydrogenation catalyst, in combination with $ZnCl_2$ as both a Lewis acid catalyst and a molten salt reaction medium, as depicted in Fig. 13. Isosorbide is of interest as an industrial monomer.

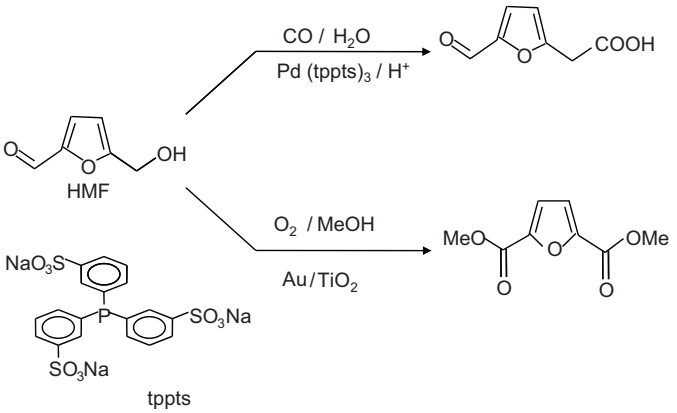

Fig. 11. Catalytic oxidation and carbonylation of HMF.

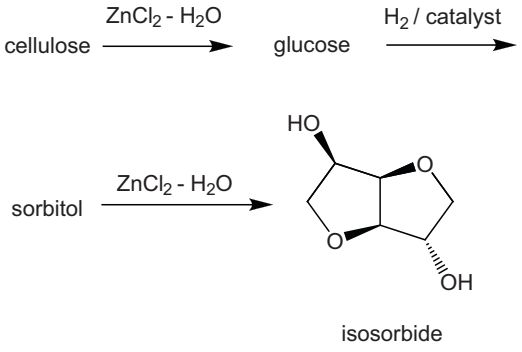

Fig. 13. One-pot conversion of cellulose to isosorbide in a molten salt medium.

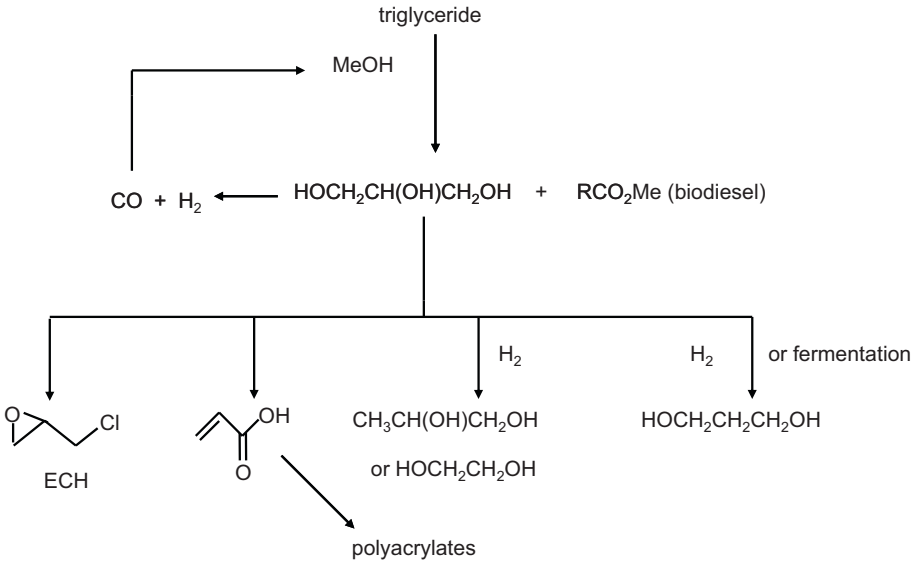

Fig. 14. Glycerol as a platform chemical.

9. Glycerol coproduct from biodiesel as a platform chemical

A direct consequence of the recent enormous increase in biodiesel production is that the coproduct, glycerol, has become a low-priced commodity chemical and an interesting raw material for other bulk chemicals such as 1,2- and 1,3-propane diol by reduction and acrylic acid by catalytic oxidation, respectively [68,69]. It can also be used for the production of epichlorohydrin (ECH) by reaction with HCl, thereby affording substantial reductions in the formation of chlorinated byproducts inherent to conventional processes for ECH manufacture. Alternatively, it can be converted, *via* syn gas to methanol for recycling to the transesterifcation of the triglyceride. Currently the glycerol is also being used as an alternative fermentation feedstock to glucose, in particular for the production of 1,3-propane diol. The various possibilities are outlined in Fig. 14.

10. Utilisation of biomass for the production of greener products

The above discussion is focused on the utilisation of biomass for more sustainable, greener processes for the manufacture of existing commodity chemicals, generally high volume industrial monomers. Alternatively, the switch to renewable raw materials could represent a golden opportunity to substitute existing products by greener products, e.g. biobased polymers from renewable feedstocks. A green sustainable product should ideally be non-toxic, biodegradable and be produced in a green catalytic process from renewable raw materials. It could be achieved by direct transformation of a biopolymer feedstock such as cellulose, starch or chitin, to a new, greener product or by its initial degradation to a platform chemical followed by conversion of the latter into a new product. A pertinent example of direct transformation is provided by carboxy starch, a biodegradable water super absorbent being touted as a replacement for the poorly biodegradable polyacrylates currently used. Carboxy starch can be produced by TEMPO (tetramethylpiperidinyoxyl radical) catalyzed hypochlorite (household bleach) oxidation of starch. A greener process would be obtained by substituting the NaOCl with molecular oxygen. This is possible using laccase as a cocatalyst but the process (Fig. 15) is not commercially viable owing to high enzyme costs. The latter are a direct result of the low operational stability of laccase under the oxidizing reaction conditions probably caused by oxidation of reactive NH_2 moieties on the exterior surface of the enzyme. We showed that the operational stability of laccase could be improved significantly by immobilization as a cross-linked enzyme aggregate (CLEA) [70].

Examples of potentially interesting platform chemicals that are designed to produce new polymers are provided by the earlier mentioned FDCA and 2-pyrone 4,6-dicarboxylic acid. The latter can be produced from lignin-derived feedstocks [71].

11. Biobased platform chemicals: towards a New Elan

Based on the above discussion of the various possibilities we would like to propose a new core of biobased platform chemicals, derived from lignocellulosic feedstock in the biorefineries of the future. First, *four lower alcohols* – methanol, ethanol, 1-butanol and isobutanol – produced either by fermentation, or in the case of methanol, *via* syn gas. The C2 and C4 alcohols can be

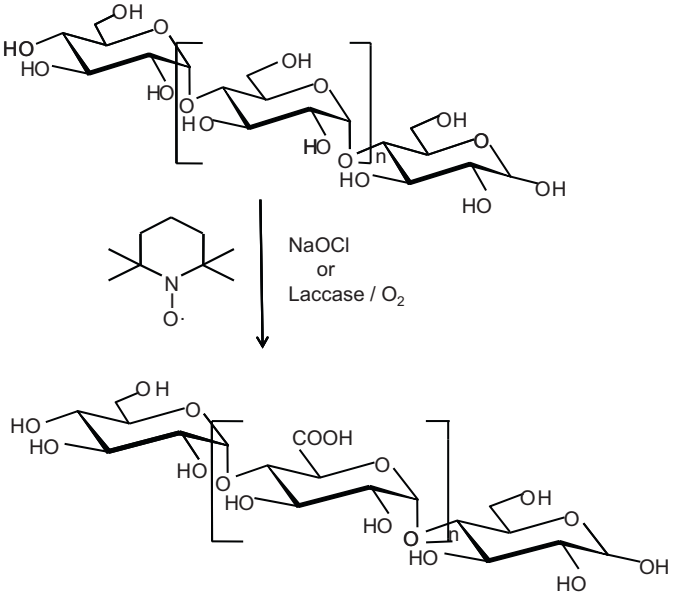

Fig. 15. Carboxy starch a biodegradable water super absorbent.

dehydrated to ethylene, 1-butene and isobutene and, *via* olefin metathesis to propylene and higher olefins, and ethanol can be easily converted to butadiene, thus providing an important link with the current petrochemical industry. Second, *three diols* – 1,2-ethane diol, 1,2-propane diol and 1,3-propane diol – produced by fermentation or chemocatalytic processes from glycerol, sorbitol or glucose, the latter being produced directly from cellulose by depolymerisation. 1,4-Butanediol could be added to the list if produced by fermentation but it is likely that it will be produced by hydrogenation of succinic acid, another platform chemical. The viability of glycerol as a platform chemical is rather uncertain as it is dependent on the future of biodiesel. Third, *two polyols* – sorbitol and xylitol – derived from cellulose and hemicellulose, respectively. Sorbitol can be easily converted to isosorbide which is likely to become an important monomer in the future. Fourth, *four carboxylic acids* – acetic, lactic, succinic, and 3-hydroxypropionic acids – from fermentation. In addition to these thirteen biobased building blocks, the list could be further broadened to include a *furanic*, *one* or more *amino acids* and possibly the hydrocarbon, isoprene as platform chemicals. We note that long chain hydrocarbons, produced by fermentation or gasification and subsequent Fischer–Tropsch synthesis, could also become platform chemicals. One class of platform chemical is clearly missing from the list: aromatics. Lignin, derived from the lignocellulose feedstock, is the obvious source of aromatics and this accounts for the current surge of interest in lignin valorization [72]. Specific platform molecules have not yet emerged but in order to generate the commodity chemicals that are required for existing products of the petrochemical industry some form of catalytic hydrodeoxygenation to simple aromatic hydrocarbons will be required. Aromatic amino acids, derived from the protein fraction of biomass or produced by fermentation, could also be a source of certain aromatics such as styrene or, alternatively, butadiene produced from bioethanol could be converted to aromatics by known technologies [27].

12. Summary and future outlook

Hopefully we have shown that there are a variety of potentially attractive catalytic methodologies, both bio-and chemocatalytic, for the utilisation of lignocellulosic biomass for the sustainable production of liquid biofuels and platform commodity chemicals. It is clear that, in order to enable the assessment of the sustainability of different methods, meaningful metrics need to be developed. It is also clear that one simple metric is probably not sufficient to evaluate both biofuels and commodity chemicals, mainly as a result of the much greater volumes and different product features required with the former. On the basis of the current state of the art we have attempted to make some predictions regarding the core group of basic chemicals that will be produced in the biorefinery of the future. We believe that chemicals production will be largely driven by biofuels production, as it is in an oil refinery, and will involve a maximum technological synergy with the current petrochemical industry in order to provide for a smooth transition from the oil-based to the renewable biobased refinery. With this in mind we suggest that the following molecules will comprise the core chemical products of lignocellulosic biorefineries. Four lower alcohols (methanol, ethanol, 1-butanol and isobutanol), produced either by fermentation or from biomass-derived syn gas, three diols (1,2-ethane diol, 1,2 propane diol and 1,3-propane diol), produced by fermentation or chemocatalytically from sorbitol, glucose or glycerol, and two polyols, sorbitol and xylitol, from hydrogenation of cellulose and hemicellulose, respectively, together with four (di)carboxylic acids (acetic, lactic, succinic and 3-hydroxypropionic acids). This core of thirteen basic chemicals may be complemented by one or two key furanic molecules such as furfural and HMF or GVL, a couple of natural amino acids, such as glutamic acid and lysine and a biohydrocarbon, such as isoprene.

In the European Union a new COST Action – Utilisation of Biomass for Sustainable Fuels and Chemicals (UBIOCHEM) – has been launched with the aim of coordinating scientific and technological innovation and mobilising a multidisciplinary effort to effect the transition from a non-sustainable economy based on finite fossil feedstocks to a sustainable one based on lignocellulose as renewable biomass. We believe that this will be achieved by the application of green, innovative and economically viable catalytic technologies. This will also require the development of meaningful metrics for assessing the sustainability of the different products and the processes to make them. We do not profess to have provided the final answer to the question of metrics, but hopefully, we have identified key issues and provided a platform for further discussion.

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