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Direct routes from biomass to end-products

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ABSTRACT

The different strategies to achieve a sustainable conversion of biomass to bioproducts will be examined. Whereas biomass conversion is widely envisioned to proceed via platform molecules that are employed as building blocks to produce chemicals, an alternative value chain is proposed that proceeds via more direct and cost effective routes and do not necessarily duplicate chemicals currently produced from fossil resources. Biopolymers such as starch or cellulose as well as plant oils can be converted in one or few steps to a mixture of molecules that can be used without further separation for the manufacture of high tonnage end-products such as paper, paints, resins, foams, lubricants, and plasticisers, that do not require the use of isolated, pure molecules. This process-driven approach will be illustrated by examples taken from literature data and results from our laboratory.

1. Introduction

Biomass conversion to biofuels and bioproducts stirred a growing interest in the last few years although R&D was more directed to biofuels than to chemicals and materials. Interest in biofuels is driven by environmental concern (greenhouse gas reduction) and economic issues (renewable carbon source). These incentives are of less importance for chemical production because of the much smaller tonnages of fossil fuel involved. However, additional incentives are currently arousing interest in the production of bioproducts from biomass, viz.:

(i) The synthesis of new products with unique properties which do not have synthetic counterpart (e.g., functional biopolymers obtained by chemical modification of natural polymers such as starch and cellulose).
(ii) The synthesis of high-added value products with “bio” or “natural” label, very attractive for marketing purpose (e.g., biodegradable surfactants, detergent builders, etc.).
(iii) The synthesis of products exempted from strict legislative constraints. Thus natural polymers even chemically modified and corresponding monomers are exempted from REACH regulation.

In the present concept article the main challenges paused by the catalytic conversion of biomass to bioproducts and the different strategies to achieve sustainable and cost-effective conversion processes will be examined. Stress will be laid on a process-driven value chain consisting of a direct conversion routes to end-products. Its potential advantages will be compared to the more conventional product-driven approach involving a multi-step conversion of platform molecules.

2. Main challenges in the synthesis of bioproducts

2.1. Feedstock availability

Renewable raw materials for chemical synthesis should be selected primarily according to their chemical structure to make them suitable for the targeted applications. Thus, terpenes are essentially suitable for the production of flavours and fragrances, fatty compounds for the production of oleochemicals and lignin for the production of phenolic compounds, while carbohydrates offer a much larger field of applications.

Another major criterion for the choice of raw materials is their availability and cost because the targeted production of bioproducts should be commensurate with available resources. Starch and other polysaccharides obtained from food crops provide a large source of C_6 sugars. Furthermore they could be replaced in the near future by cellulose which will provide an almost unlimited source of C_6 without affecting food needs. In the same way hemicellulose, which is more easily depolymerised than cellulose, provides a potentially large source of C_5 sugars. Vegetal proteins and aminoacids obtained as co-products of carbohydrate fermentation to bioethanol could become a significant resource in the future [1].

In contrast with carbohydrates, the production of triglycerides from plant oils is much lower (ca. 130 MTon/y) and there is competition between food needs and industrial applications (about 110 and 20 MTon/y, respectively). In addition there is a severe competi-

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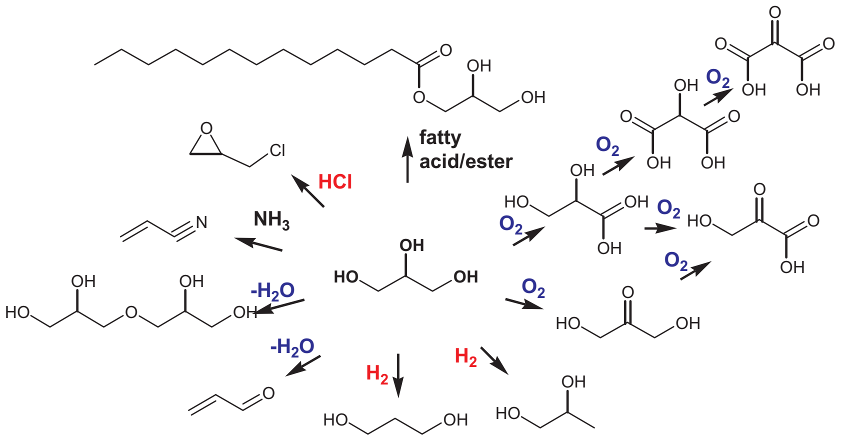

Fig. 1. Selected examples of catalytic conversion of glycerol to chemicals.

tion between biodiesel and oleochemical production (surfactants, lubricants, plasticisers, polymers) which is biased by governmental subsidising policies beneficiating to biodiesel only [2]. Unless new sources of triglycerides become available (e.g., from progress in algae production and processing) biodiesel and oleochemical production could not expend to a large extent.

Glycerol is a case study to illustrate the fact that targeted applications could be limited by feedstock availability. As a co-product of biodiesel manufacture from seed oils glycerol production cannot grow beyond a few million tons. Still, glycerol is a wonderful platform molecule from which many useful intermediates or specialty chemicals can be produced [3]. A few catalytic reactions of industrial interest are depicted in Fig. 1. Solvay is planning to use glycerol for the synthesis of 100 000 Ton/y of epichlorohydrine [4] and ADM is starting a plan to produce similar amounts of propylene glycol [5]. A demonstration plant for the production of acrolein and acrylic acid by dehydration of glycerol was also invoked [6]. These future outlets will add up to the existing thousand applications of glycerol in food or feed ingredients, cosmetics, pharmaceuticals, explosives, etc. As the demand is increasing the market price of high grade glycerol will stay at a level hardly compatible with an economic production of large volume of intermediates so it may be wiser to target high value added chemicals.

2.2. R&D strategies for catalytic conversion processes

Cost effective processes adapted to the molecular structure of highly functionalised biomass molecules have to be developed to make the quality and price of chemicals competitive with respect to products obtained by traditional routes from fossil fuels. Flexible catalytic processes are needed to cope with variations in feedstock availability and molecular structure. Robust and easily regenerated catalysts should be developed because natural raw materials may contain impurities which could alter their selectivity and decrease their activity thus hampering catalyst recycling or continuous processes. New reaction media such supercritical fluids and activation systems (ultrasounds, microwaves) should be employed. Biomass conversion processes should follow the principles of green chemistry to minimise waste and energy which is not the case in many current investigations where the green character of reaction medium and catalytic system is questionable.

Finding the best pathway to convert biomass into a given biofuel is comparatively straightforward because target and feedstock are well identified so that only the conversion technology remains to be selected and optimised. Thus, biodiesel can be produced from plant oils by optimising transesterification, hydrotreatment or decarboxylation reactions (Fig. 2). As pinpointed by Bozell and Petersen [7] the situation is more complex for chemicals because there is an abundance of potential targets that can be obtained by different reactions starting possibly from different feedstocks (Fig. 2).

Two different strategies can be chosen to achieve a sustainable biomass conversion, viz.:

(i) Select a target molecule and find the most efficient synthesis flow-sheet starting from a given feedstock. This product-driven approach is the most widely envisioned R&D strategy, but it may need laborious development and result in uneconomical processes with respect to existing synthesis route from hydrocarbons.
(ii) Select a process based on a given catalytic reaction (hydrogenation, hydrogenolysis, oxidation, etc.) capable of converting renewable biopolymers with a high yield to one or more products. Applied at the research stage, it could be more effective to find rapidly an efficient pathway to a valuable product and thus contribute to a faster development of biomass use. Still, a market has to be found for the resulting reaction products.

3. Conversion of biomass via platform molecules

The production of chemicals from biomass is widely envisioned to proceeds in a biorefinery scheme whereby carbohydrate biopolymers are converted by depolymerisation and/or fermentation steps into platform molecules that are subsequently employed as building blocks for the synthesis of intermediates and fine chemicals via heterogeneous and/or homogenous catalytic processes (Fig. 3). This product-driven value chain has been widely publicised in the literature published since the 2004 US DoE report identifying top 10 platform molecules derived from carbohydrates and their possible derivatives [8].

The value chain is quite comparable to traditional synthesis route from hydrocarbons whereby pure compounds are produced via a multi-step flow sheet involving isolation of intermediate and final products. The processes can easily be scaled up in existing chemical plants. This value chain is mostly envisioned to pro-

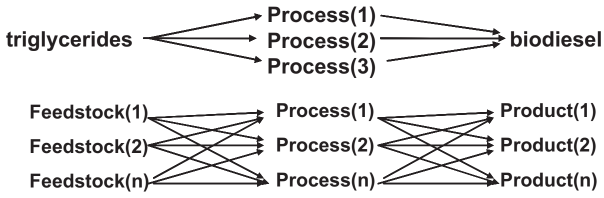

Fig. 2. Comparison of the value chains for biodiesel and bioproducts.

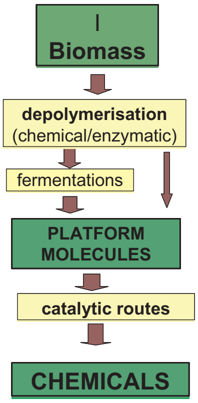

Fig. 3. Biomass conversion to isolated pure chemicals via platform molecules.

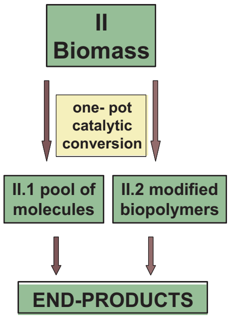

Fig. 4. Direct route from biomass to end-products.

duce chemicals that have already a market so that the commercial and marketing operations are easily integrated in business plans. There are many examples of industrial achievements in existing starch biorefinery (e.g., Roquette in Europe or Cargill in the USA) or plant oil biorefinery (e.g., Cognis in Germany). Interestingly the successful developments consist often of new products rather than existing chemicals such as alkylpolyglucoside surfactants, PLA polymer and isosorbide used as green solvent and building block for surfactants and plasticisers. The production of chemicals that have already a market experiences a severe economic competition with conventional synthesis routes from hydrocarbons that have been optimised steadily over one century.

Another factor affecting the process economy of this value chain is the degree of purity of platform molecules used as building blocks for the synthesis of pure compounds. Thus, carboxylic acids obtained by fermentation of carbohydrates contain a number of impurities which have to be removed by costly downstream processing. Even so, the remaining traces of impurities could inhibit the activity of catalysts used for subsequent conversions, which requires the development of robust catalysts or regeneration processes. Thus, succinic acid produced by fermentation from carbohydrates requires downstream processing before further catalytic conversion [9]. Also glycerol obtained as a co-product of biodiesel should be subjected to costly purification before being used in chemical synthesis [10], but the degree of purity is insufficient to meet specifications for cosmetic and pharmaceutical applications which still rely on synthetic glycerine produced by DOW chemicals [11].

4. Direct biomass conversion routes to chemicals

An alternative value chain consists of converting biomass in one or two steps to a mixture of molecules that are used as such for the manufacture of end-products [12,13]. This process-driven approach is quite different from traditional chemical synthesis involving multi-step process with isolation of intermediates and final products and it is not intended to duplicate chemicals currently produced from fossil resources. Accordingly, plant oils or carbohydrates including biopolymers (starch, cellulose, hemicellulose) are converted via one-pot catalytic process yielding a mixture of molecules with similar functionalities. The pool of molecules can be used without further separation for the manufacture of high tonnage end-products such as paper, paints, resins, foams, lubricants, plasticisers, and cosmetics, that do not require the use of isolated, pure molecules (route II.1, Fig. 4). Alternatively, polysaccharides could be submitted to catalytic modifications aimed at introducing new functionalities along the biopolymer backbone without breaking polymeric chains. The functional biopolymers thus obtained can be used to manufacture high tonnage end-products and materials that have no synthetic counterpart (route II.2, Fig. 4). Selected examples of this process-driven approach are given hereafter to illustrate the potential benefits this more direct route to valuable end-products.

4.1. *End products from a pool of molecules*

The molecular structure of plant oils is based on a pool of unsaturated C_{18}, C_{16}, C_{14}, C_{12}, and C_{10} fatty esters that can be converted to lubricants, plasticisers and polymers in one or two steps. Thus, Hölderich et al. [14] succeeded in preparing biodegradable lubricants meeting specifications in two steps including epoxidation of the C=C bonds with TBHP followed by epoxidation aperture with methanol in the presence of Nafion or Amberlyst15 catalysts. More recently epoxidised plants oils were converted by acylation in the presence of homogeneous or heterogeneous catalyst to prepare non-toxic PVC plasticisers aimed at replacing phthalates which are banned for a number of applications [15]. The bioplasticisers obtained with a 70% yield were shown to meet the required rheological specifications for flexible PVC. Plant oils are converted to a mixture of polyols by various reactions (epoxidation/ring opening, hydroformylation/hydrogenation and ozonolysis) used for the synthesis of polyurethane foams by reaction with polyisocyanates [16]. Cargill is currently producing polyols (BiOH®) that are used for the growing market of flexible foams.

Because of their much larger availability and lower cost carbohydrates polymers are well suited to prepare polyol mixtures. Within a consortium involving our laboratory, Degussa and ICI paints, starch hydrolysates were converted to a mixture of polyols suitable for the synthesis of polyesters and alkyd resins employed for decorative coating applications. In a first route depicted in Fig. 5, sorbitol and mannitol solutions, obtained by combined hydrolysis/hydrogenation of starch hydrolysates on a bifunctional Ru/HY catalyst, were dehydroxylated on a CuO–ZnO catalyst at 180 °C under H_2-pressure yielding a mixture of C_4–C_6 diols, triols and tetrols containing 63% of deoxyhexitols [17]. Alternatively, in the presence of 3 wt% Pd/C catalyst, sorbitol solutions acidified with propionic acid were cyclodehydrated to a mixture of cyclic ethers containing 38% of isosorbide, and 58% of tetrols (2,5-anhydromannitol, 1,4-anhydrosorbitol and 2,5-anhydroiditol) [18]. The mixtures of polyols obtained either by dehydroxylation or by dehydration were successfully employed without any further separation or purification to substitute pentaerythritol and other polyols derived from fossil resources for the manufacture of alkyd resins meeting the specifications required for coating applications.

Polyol blends derived from cellulose conversion or even from wheat straw were used for the manufacture of polyurethane foams [19]. Hemicelluloses that are easier to depolymerise than cellulose provide a blend of hexoses and pentoses. Thus, the depolymerisation of araboxylan-containing hemicellulose yielded a syrup

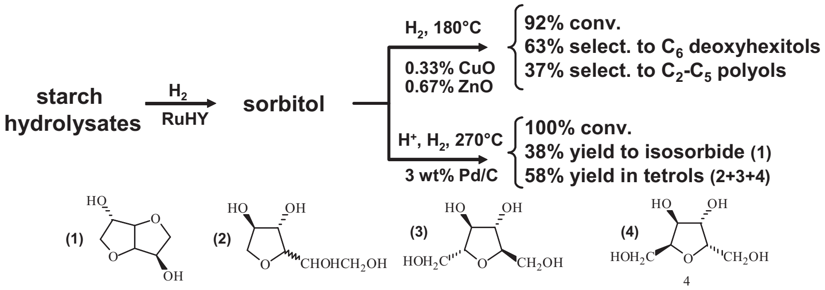

Fig. 5. Conversion by dehydroxylation [17] or cyclodehydration [18] of sorbitol obtained via one-pot hydrolysis/hydrogenation from commercial starch hydrolysates.

containing a mixture of various pentoses which was reacted with butadiene in the presence of soluble palladium complexes which catalyse the telomerisation of butadiene on alcohol functions. The resulting mixture containing 67% mono-octadienyl and 31% dioctadienyl pentosides provided a low-cost, biodegradable surfactant exhibiting a surface activity comparable to that of molecularly pure commercial surfactants [20].

Marinkovic and Estrine [21] succeeded to achieve an acid-catalysed, one-pot conversion of hemicellulose involving the hydrolysis to pentoses followed by acetalisation with fatty alcohols. The resulting mixture of alkyl-glucosides, -xylosides, and -arabinosides could be used as a very cheap biodegradable surfactant (Fig. 6).

4.2. End-products from modified biopolymers

Chemically modified celluloses have been used for more than a century to produce functional materials. Cellulose ethers (methoxyl-, ethoxyl- and hydroethoxylcellulose) and esters are still employed today as coating agents, films, drilling fluids membranes, cosmetics, and food additives (stabiliser or extrusion aid). The chemical modification of biopolymers is presently a vivid field of research which was the subject of recent reviews [22–24]. Modifications of starch backbone were studied particularly to produce paper additives [25]. More recently, hemicellulose [24] and vegetal proteins [26] were subjected to chemical modifications to produce biocompatible films and coatings.

The following examples deal with catalytically assisted oxidation and etherification reactions of polysaccharides (route II.2, Fig. 4). Starch and other polysaccharides have been oxidised with the NaOCl/NaBr oxidising system in the presence of TEMPO radical (2,2,6,6-tetramethylpiperidinine-1-oxyl) [27]. The system was very selective to oxidise the primary alcohol function at C_6 position with a 98% yield with minor chain breaking. The oxidised biopolymers can be used as thickeners, stabilisers, super-adsorbents, sequestering agents and detergent builders. TEMPO-mediated oxidation has been recently extended to cellulose. Isogai et al. [28] have shown that cellulose from bleached Kraft pulp can be converted by selective oxidation to materials employed as transparent gas barrier films for packaging or in high tech applications such as flexible display panels (Fig. 7).

An efficient catalytic system for the selective oxidation of biopolymers has been designed by Sorokin et al. [29–31]. Insoluble, native starch was oxidised with H_2O_2 in the presence of water-soluble, iron tetrasulfophthalocyanine complex to obtain more hydrophilic starch without major chain breaking (Fig. 8).

The oxidation was best achieved by incipient wetness method whereby catalysts dissolved in small volumes of water was impregnated in starch powder under continuous mixing, followed by addition of hydrogen peroxide to the impregnated solid. The hydroxyl groups of anhydroglucose units were oxidised at C_2, C_3 and C_6 positions into carbonyl and carboxyl functions. Typically, with a substrate/catalyst ratio of only 25,800/1 the oxidation yielded 1.5 carboxyl and 5.6 carbonyl functions per 100 glucose units. The process was applied to starches obtained from dif-

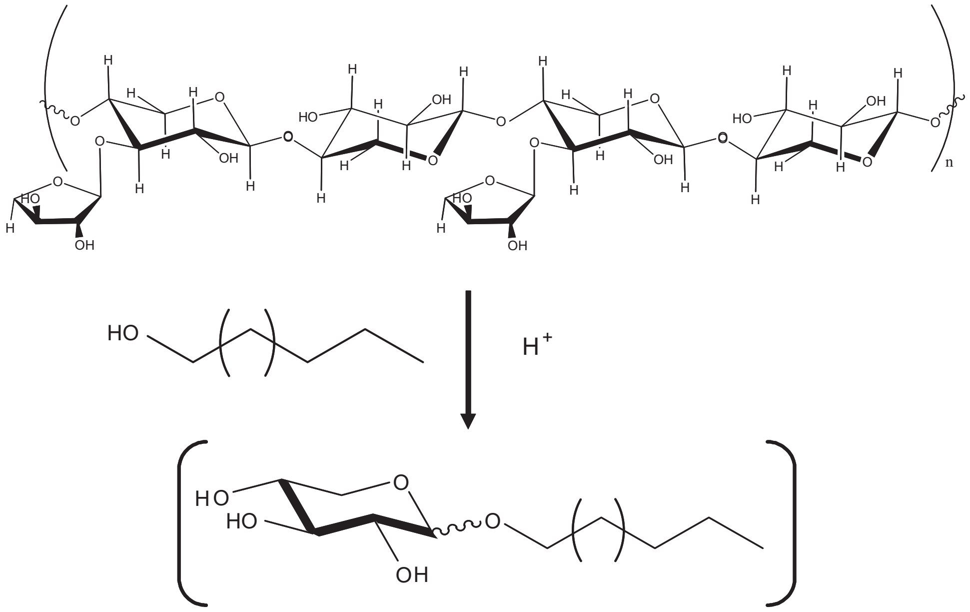

Fig. 6. One-pot synthesis of alkylpentoside mixture from hemicellulose and fatty alcohols.

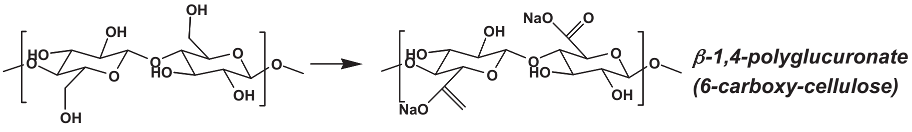

Fig. 7. TEMPO-mediated oxidation of cellulose.

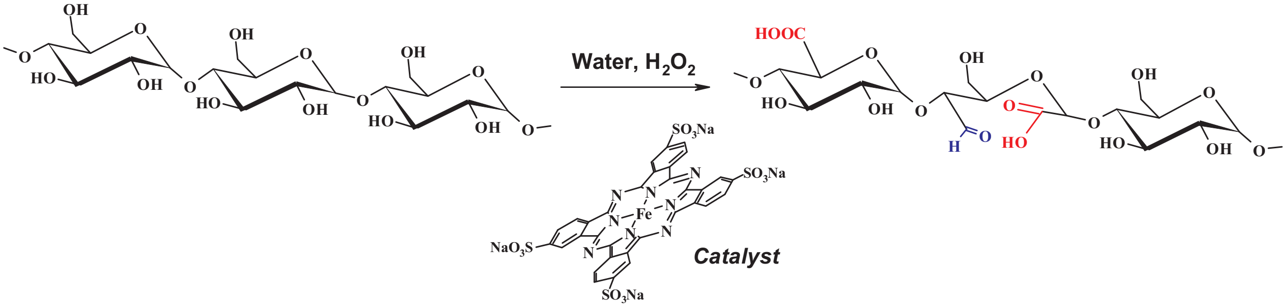

Fig. 8. Fe-phthalocyanine-mediated oxidation to hydrophilic starch.

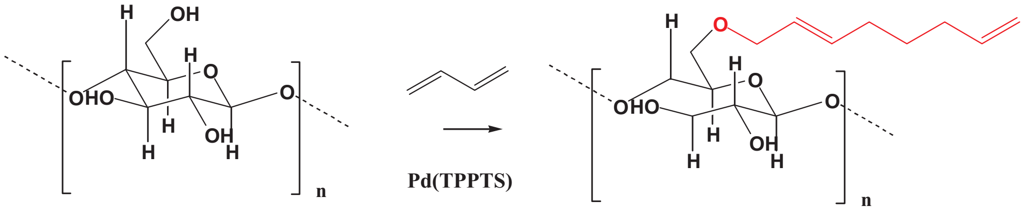

Fig. 9. Telomerisation of butadiene to hydrophobic starch.

ferent crops (potato, wheat, rice, corn) and it was extended to cellulose, inulin and guar gum, giving a high degree of substitution (e.g., up to $DS_{COOH} = 26.5$ and $DS_{CHO} = 11.6$ for cellulose) [31]. The modified polysaccharides were successfully tested for various applications particularly for the formulation of coating agents and cosmetics.

Whereas biopolymer hydrophilicity is increased by selective oxidation, inversely it can be decreased by grafting hydrocarbon chains on the hydroxyl groups of the polymer backbone. Stoichiometric etherification or esterification reactions have been employed in the past but a new route consisting of grafting octadienyl chains on biopolymers by butadiene telomerisation has been designed by Pinel et al. [32–34]. The reaction was catalysed by hydrosoluble palladium complexes prepared from palladium diacetate and trisodium tris(m-sulfonatophenyl)phosphine (TPPTS). This reaction produces no salt and has the advantage to be 100% atom-efficient (Fig. 9).

This reaction was challenging because native starch is insoluble in water and gelatinises at temperature higher than ca. 70 °C. The degree of substitution (DS) should be kept low enough because modified starch should not be too hydrophobic, and for obvious economical reason the catalyst/starch ratio should be kept low. Modified starch with DS = 0.06 obtained with 0.03% palladium at 50 °C meets specification for use as thickener for decorative paints. No palladium was detected in the modified polymer when the reaction was conducted in the presence of 0.05% palladium. The process was improved by using H_2O-dimethylisosorbide or H_2O-isopropanol solvent in the presence of Na_2SO_4 and $[(\pi\text{-allyl})Pd(TPPTS)_2]Cl$ catalytic system [33]. A further improvement was achieved by conducting the reaction in an isopropanol-free reaction medium by adding minute amounts of surfactants allowing the dispersion of butadiene micelles in water [34].

5. Conclusion

There are many other examples in the literature, particularly in recent patents which could not be discussed in this brief survey, of biomass conversion via one-pot catalytic process to end-products. This process-driven approach yields chemicals that do not duplicate those currently produced by traditional synthesis routes from fossil fuels. Blends of molecules with similar functionalities such as polyols or fatty compounds, or chemically modified biopolymers, can be used without further separation for the manufacture of high tonnage end-products such as paper, paints, resins, foams, lubricants, and plasticisers, that do not require the use of isolated, pure molecules. This value chain is environmentally and economically sustainable because it requires only a small number of conversion steps from raw biomass to end-products. One-pot processes could lead to a faster development of biomass utilisation for the manufacture of industrial products while conversion processes via platform molecules have to compete with well-established current processes for the production of isolated, pure chemicals.

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