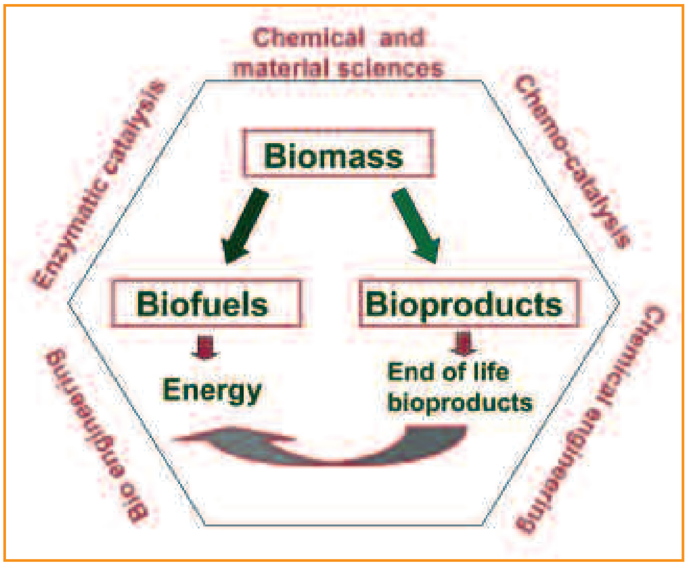

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NEW STRATEGIES AND CATALYSTS FOR THE CONVERSION OF BIOMASS TO BIOPRODUCTS

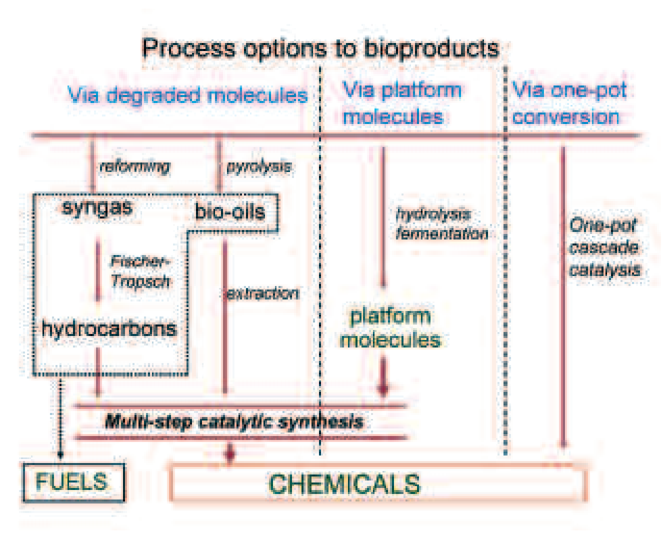
This paper evaluates the relative advantages of different process options to convert renewables into chemicals. Three process options that can be integrated in a biorefinery scheme are illustrated by selected examples. Stress is laid on processes involving one-step catalytic conversion to products.

The use of biomass for the production of energy, chemicals and materials is a key issue of sustainable development. Indeed, bioresources are renewable and CO_2 neutral in contrast with fossil fuels. Furthermore the market price of biomass-derived molecules such as sucrose or glucose is now comparable than that of crude oil and it was fairly stable over a long period of time. The implementation Action Plan 2006 [1] of the European SusChem organisation recommends the use of renewables as alternative feedstocks for fuel and chemical production. There is an additional benefit of using renewable feedstocks because the molecules extracted from bio-based resources are already functionalised so that the synthesis of chemicals may require a lower number of steps than from hydrocarbons. Also, bio-based products have unique properties such as biodegradability and biocompatibility. On a mere economical ground, products issued from biomass have a higher added value and their marketing is made easier because of their "natural" or "bio" label.

There is a severe competition for the production of food/feed, bioproducts (chemical and polymers) and transportation biofuels (bioethanol and biodiesel) from agricultural crops. Conventional crops based on cereals and seed oils could only be a partial answer to the fuel issue because of the huge needs at stake. To meet biofuel and chemicals demands in a more substantial way, it is recommended [1] to process agricultural wastes, new crops grown on marginal land, and fast-growing vegetative biomass (grass, wood, stems, leaves, etc.) consisting of cellulose and

ligno-cellulose rather than using seeds (cereals and vegetable oils).

Various hurdles may hamper the development of renewables for bio-product production. The main issue is the high cost involved in processing renewable feedstock to chemicals. Processes employed for the synthesis of chemicals from fossil fuels improved continuously during more than a century resulting in a very high degree of technical and cost optimisation. In contrast, processes to derive chemicals from biomass are comparatively in infancy and their cost weights heavily on the market price of bioproducts. Alternative value chains have to be developed to reduce the biomass processing cost, by designing catalytic routes different from those employed from hydrocarbons and adapted to the specific molecular structure of biomolecules. It is mandatory to carry out life cycle analysis to verify the sustainability of processes starting from renewable feedstocks and to assess the benefits of employing biomass rather than fossil fuels to prepare a given chemical. Socio-economic studies should also be performed to assess the societal impact of intensive agricultural activities covering large land areas, increasing the water stress and impairing biodiversity.



Scheme of the possible process options to transform biomasses

The present paper will focus on process options that could be integrated in a biorefinery. The underlying idea is to maximise the value derived from biomass by producing energy and multiple products via well integrated processes, valorising co-products and by-products, optimising the inputs (feedstock supply, water management) and outputs (energy and product recovery, treatments of waste. Large biorefineries for carbohydrate processing to bioproducts are currently operating in Europe (e.g., Roquette bio-hub at Lestrem, France). Similarly the production of oleochemicals and biodiesel can be integrated in biorefineries using vegetables oils as main feedstock.

Process options for biomass conversion to bioproducts

Within the biorefinery scheme several processing options of renewables feedstocks can potentially be employed to produce bioproducts. The Figure gives a simplified scheme of the process options discussed and illustrated by selected examples in the following sections.

From biomass to products via degraded molecules

Biomass derivatives can potentially be converted to synthesis gas by adapting well known steam or autothermal reforming processes leading to syngas. Syngas is then converted via Fischer-Tropsch synthesis to methanol or hydrocarbons which are subse-

quently converted to chemicals via usual synthesis routes developed for petroleum feedstock. This approach has been little developed particularly for the production chemicals. The overall sustainability and economy of the value chain - biomass to chemicals via gasification - is doubtful or need to be validated by life cycle analysis. A more appealing route consists of performing aqueous phase reforming of sugar-derived polyols yielding directly alkanes [2-4]. However, the reforming of renewables should rather be conducted with organic wastes or vegetative biomass rather than with high priced molecules. Another approach to produce chemicals via degraded molecules is the fast pyrolysis of biomass [5, 6]. Valuable compounds present in bio-oils, particularly phenolic compounds issued from the degradation of lignin can potentially be recovered [7, 8].

From biomass to products via platform molecules

As far as carbohydrates are concerned a number of platform molecules are already well identified and currently employed to synthesize specialties and fine chemicals. Monosaccharides such as glucose and fructose and disaccharides such as sucrose are easily obtained by hydrolysis from various crops. Platform molecules are also obtained via fermentation of carbohydrates, e.g., ethanol and acids such as aspartic, succinic, fumaric, malic, glutamic, glucaric, 2,5-furandicarboxylic, 3-hydroxypropionic, 2-hydroxy propionic, itaconic, and levulinic acids. In the future the challenge will be to produce fermentable sugars from cellulose and hemicelluloses that are available in huge amounts from vegetative biomass. Fatty acid esters and derivatives (fatty acids and alcohols) produced from vegetable oils and terpenes such as α- and β-pinenes, which are extracted from turpentine oil, are also valuable platform molecules for chemical synthesis. A few selected examples of catalytic conversions of platform molecules are given hereafter.

Carbohydrates

The catalytic conversion of sugars has been reviewed by van Bekkum and Besemer [9] and by Lichtenthaler and Peters [10]. The hydrogenation of 40 wt% water solution of glucose was performed in trickle-bed reactor on 1.8% Ru/C catalysts [11]. The catalyst was highly stable since after 596 h on stream the selectivity to sorbitol at total glucose conversion was 99.3%. The oxidation of glucose to gluconic acid was achieved quantitatively on PtBi/C catalysts (yield> 99%); the catalysts was recycled many times with negligible loss of activity and selectivity [12].

There is a great interest to convert C_6 molecules available in large supply from biomass into C_5 and C_4 polyols that find many applications in food and non-food products. Thus, glucose can be converted to arabitol by an oxidative decarboxylation to arabinonic acid which is subsequently hydrogenated to arabitol. The main pitfall is to avoid dehydroxylation reactions leading to deoxy-products not compatible with purity specifications required for arabitol. Aqueous solutions (20 wt%) of arabinonic acid were hydrogenated on Ru-catalysts promoted by small amount of anthraquinone-2-sulfonate yielding 98% of arabitol [13].

Lactic (2-hydroxypropionic) acid obtained by fermentation of saccharides is employed by NatureWorks (Cargill/Dow LLC) to produce polylactide (PLA) a biodegradable or recyclable polymer with a potential production of 140,000 t/y [14]. 3-hydroxypropionic acid obtained by fermentation of glucose could also be a good candidate to produce various chemicals by catalytic routes [15]. R&D is actively conducted at DuPont Co. to employ levulinic acid derived from cellulose for the synthesis of solvents and surfactants, polymers and fuel additives [16].

The catalytic routes to obtain chemicals and polymers from furan derivatives have been reviewed by Moreau *et al.* [17]. Fructose dehydration to *5*-hydroxymethylfurfural (HMF) was performed at 165 °C in the presence of dealuminated mordenite (Si/Al=11) with a selectivity of 92% at 76% fructose conversion [18]. Starting from inulin hydrolysates the selectivity to HMF was up to 97% at 54% conversion [19]. The hydrogenation of HMF in the presence of metal catalysts leads to quantitative amounts of *2,5*-bishydroxy methylfuran used in the manufacture of polyurethanes, or *2,5*-bishydroxymethyltetrahydrofuran which can be used in the preparation of polyesters [20]. The oxidation of HMF on Pt-catalysts yielded quantitatively *2,5*-furandicarboxylic acid a potential substitute of terephtalic acid [21].

Fatty acid esters and fatty alcohols

Fatty acid esters of glycerol are efficient surfactants obtained either by transesterification of triglycerides with glycerol (glycerolysis) or by esterification of fatty acids with glycerol. Glycerolysis of rapeseed oil on MgO catalysts yielded 63% of monoglyceride [22].The synthesis of glycerol monoesters by esterification of fatty acids with glycerol was achieved with various acidic solids to substitute sulfuric acid [23-27]. Alkylglucosides are obtained by acetalisation of carbohydrates with fatty alcohols in the presence of acid catalysts. Zeolites and MCM-41 have been used as acidic catalysts with shape selectivity effect to achieve glucose acetalisation with alcohols [28].

The epoxidation of a mixture of FAME from sunflower oil was achieved with *tert*-butylhydroperoxide (TBHP) at 363 K in the presence of Ti-MCM-41 catalysts yielding 85% of mono-epoxy compounds [29]. Rios *et al.* [30] using Ti-MCM-41 and amorphous Ti/SiO_2-catalysts achieved methyl oleate epoxidation with TBHP at 70 °C with selectivities higher than 95% providing titanium was well dispersed. The methanolysis of epoxidized methyl oleate at 60 °C in the presence of Nafion entrapped in silica or of Amberlyst15 resin resulted in selectivities higher than 98% at total conversion [31]. Catalytic C-C coupling reactions of unsaturated fatty compounds have been reviewed by Biermann and Metzger [32]. Metathesis reactions involving unsaturated fatty compounds to prepare ω-unsaturated fatty acid esters were applied by Warwel *et al.* [33].

Glycerol

Besson and Gallezot [34] have shown that valuable oxygenates can be obtained by oxidation with air of aqueous solutions of glycerol in the presence of carbon-supported platinum and palladium catalysts. The oxidation of glycerol at basic pH on palladium and platinum catalysts yielded 70% glycerate [35]. Glyceric acid oxidation on 5%Pt-1.9%Bi/C catalyst yielded 74% hydroxypyruvic at 80% conversion at acidic pH (3-4), but on the same catalyst under basic condition (pH 10-11) a 83% yield to tartronate was obtained at 85% conversion [36]. Abbadi and van Bekkum [37] obtained 93% selectivity to hydroxypyruvic acid at 95% conversion of glyceric acid on 5%Bi-5%Pt/C catalyst without pH regulation. The selectivity of glycerol oxidation in the presence of gold catalysts in basic medium depended critically upon the size of gold particles [38-40]. Chaminand *et al.* [41] studied the hydrogenolysis of aqueous solutions of glycerol at 180 °C under 80 bar H_2-pressure in the presence of supported metal catalysts in an attempt to produce selectively 1,2- and 1,3-PDO. The best selectivity (100%) to 1,2-PDO was obtained by hydrogenolysis of water solution of glycerol in the presence of CuO/ZnO catalysts. The best selectivity to 1,3-PDO (1,3-PDO/1,2-PDO = 2) was obtained in sulfolane with rhodium catalysts promoted with tungstic acid.

Biomass to products via one-pot reactions

Multi-step reactions to targeted molecules can be carried out by cascade catalysis without intermediate product recovery. Another innovative approach consists of one-pot catalytic conversion of biomass to prepare a mixture of molecules which do not require to be isolated for the preparation of end-products such as paints, paper, construction materials etc.

Starch hydrolysates were converted by combined hydrolysis-hydrogenation in a reactor loaded with Ru/HY catalysts to sorbitol, then in a second reactor, sorbitol was converted either by dehydroxylation to C_4-C_6 products [42] or by dehydration to cyclic polyols depending upon reaction conditions [43]. Reactions carried out in the presence of 33% CuO-65% ZnO catalyst at 180 °C under H_2-pressure yielded 73% C_4^+ polyols, and more specifically, 63% deoxyhexitols. The dehydration of water solution of sorbitol carried out at 250 °C under 80 bar of hydrogen pressure in the presence of 0.5% Pd/C catalyst yielded 37.5% of isosorbide, 37.5% of *2,5*-anhydromannitol, and 25% of 1,4-anhydrosorbitol. These mixture of polyols were used to prepare polyesters for decorative paint formulation.

Native starch was oxidised with H_2O_2 in the presence of soluble organometallic complexes to meet specific hydrophilic/hydrophobic properties needed for end-products for paper, paint and cosmetic industries [44-46]. Reactions were catalysed by water soluble, iron tetrasulfophtalocyanine (FePcS) complexes, which are cheap and available at industrial scale. Starches from different origin were oxidized by H_2O_2 following two operating modes, viz.: oxidation in aqueous suspension and oxidation by incipient wetness. The oxidation of native starch by incipient wetness method was achieved by adding a small volume of water containing the dissolved catalysts to starch powder under continuous mixing, followed by addition of hydrogen peroxide to the impregnated solid under mixing. With a substrate/catalyst ratio of only 25800/1 the oxidation yielded 1.5 carboxyl and 5.6 carbonyl functions per 100 glucose units. The process was applied with success to the oxidation of starches of different physical and chemical properties (amylose/amylopectin ratio, granule size, temperature of gelatinisation) obtained from different crops (potato, wheat, rice, corn). It was further extended to cellulose, inulin and guar gum, giving a high degree of substitution. The method was scaled up to prepare 150 L of hydrophilic starch which was incorporated successfully in paint formulations. Interestingly, this is a rather unique example of heterogeneous catalytic process involving a soluble catalyst and a solid substrate.

A new route to prepare hydrophobic starch consisting of grafting octadienyl chains by butadiene telomerisation has been investigated [44, 47-49]. The reaction was catalysed by hydrosoluble palladium complexes prepared from palladium diacetate and trisodium tris(m-sulfonatophenyl)phosphine (TPPTS). The reaction conducted on sucrose gave DS of 0.5 and 5 after 14 and 64 h reaction time, respectively [47], but the transposition of this reaction to starch [44, 48] was challenging because this substrate is insoluble in water at room temperature and gelatinizes at temperature higher than *ca* 70 °C. Modified starch with DS = 0.06 obtained with 0.03% palladium at 50 °C met specifications for use as thickener for decorative paints. The etherified starch was further transformed by hydrogenation of the double bonds to yield the corresponding linear octyl groups using $[RhCl(TPPTS)_3]$ catalyst soluble in $EtOH/H_2O$ mixtures. Complete hydrogenation was obtained at 40 °C under 30 bar of H_2 after 12 h using 0.8 wt% Rh-catalyst [49].

Conclusion

Alternative value chains have to be developed to decrease the cost and to increase the quality of end-products. In view of the diversity and complexity of renewable feedstocks and of the potentially very high number of bio-products at stake, integrated eco-efficient processes should be conducted in biorefineries. We have identified three process options to produce chemicals by catalytic routes, viz.:

1) The degradation of biomass by gasification or pyrolysis leading to syngas and bio-oils, respectively. This approach provides primarily fuels rather than starting materials for bio-product synthesis.

2) The catalytic conversion of platform molecules produced by bioconversion of renewables to bioproducts. This is already the basis of many industrial processes leading to important tonnages of chemicals and polymers.

3) A much larger gain in process economy and waste minimisation should be obtained if a mixture of products suitable for a particular application, e.g., in paper, paint, construction materials and cosmetic industries, can be prepared in one pot process starting from biomass.

To meet the challenge paused by the processing of renewables, a large integrated research effort in chemistry, biochemistry, and genetics as well as in chemical and biochemical engineering will be required both in industrial and academic research centres.

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