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Catalytic routes from renewables to fine chemicals

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Abstract

This paper gives a short review of different catalytic processes for the conversion of terpenes, triglycerides and carbohydrates to valuable chemicals and polymers. Attention is focussed on the new catalytic routes starting from platform molecules derived from renewables and different from the traditional chemical synthesis routes starting from fossil fuels. Also, stress is laid on the green character of these new processes and on the possibility to conduct one-pot process whenever possible.

Keywords: Terpenes; Triglycerides; Carbohydrates; Renewables; Catalytic routes; Valuable chemicals; Polymers

1. Introduction

An increasing use of biomass for energy, chemicals and material supply is one of the key issues of sustainable development because bio-based resources are renewable and CO_2 neutral in contrast with fossil fuels. The molecules extracted from bio-based resources already contain functional groups so that the synthesis of chemicals generally requires a lower number of steps than from alkanes. Also, bio-based products may have unique properties compared to hydrocarbon-derived products, for instance biodegradability and biocompatibility. In addition, products issued from biomass get a higher added value because of the "natural" or "bio" label. The Biomass Program of the US Department of Energy [1] and the Implementation Action Plan 2006 of SUSCHEM organization in Europe [2], promote the increasing use of renewables for energy and chemical production.

However various hurdles may hamper the development of renewables as feedstock for bio-product production. Firstly, there is an increasing competition between the use of crops for food/feed, for bio-fuels (ethanol, biodiesel) and for bio-product production. Also the supply and composition of renewable raw materials is subject to change with year and location of crops. Supply issues could be solved in the future by using crops dedicated to chemical production and genetically engineered plants giving a more constant supply and suitable composition matching the desired products. Secondly, processing renewables to bio-products is presently much costlier than the conventional processes from hydrocarbons thus making bio-based products not cost-competitive. Accordingly, extensive R&D efforts in biotechnology, chemistry and engineering will be required to reduce processing cost. More specifically new catalytic routes, different from the synthesis flow sheets established for hydrocarbons, have to be designed.

Most of the non-food applications of bio-based resources fall into four categories, viz.: (i) traditional uses in timber, paper, fiber and rubber industries, and extraction of fine chemicals (flavours and fragrances, dyes, bioactive molecules); (ii) thermal power generation (bio-power) by direct combustion of biomass or after gasification; (iii) production of bio-based transportation fuels, e.g., production of ethanol by fermentation of carbohydrates, of bio-diesel by transesterification of vegetable oils, and of hydrogen by steam reforming/WGS of biomass; (iv) production of bio-based products by catalytic conversion of carbohydrates, triglycerides, terpenes and lignocellulosic materials.

The present paper will focus exclusively on item (iv), i.e., the catalytic conversion of renewables to bio-based chemicals and polymers, stress being laid on processes involving heterogeneous and homogeneous catalysts. It is not intended to give an extensive review of the subject rather selected examples of catalytic conversion will be given.

2. Strategies for biomass conversion to chemicals

The traditional synthesis flow sheets which were developed and optimised for more than a century from hydrocarbons to

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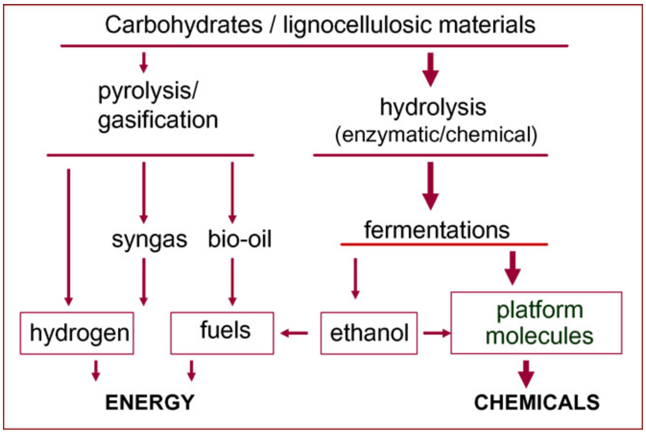


Fig. 1. Simplified scheme of biorefinery operations.

produce the great majority of existing chemicals and polymers are not adapted to renewables which are already deeply functionalised. Three types of alternative strategies can potentially be used to convert biomass into products:

(i) *From biomass to products via degraded molecules*. In this scheme, biomass is firstly converted by gasification to synthesis gas or by pyrolysis to a mixture of small molecules often called bio-oils. Synthesis gas may then be converted to hydrocarbons or methanol that are subsequently converted to intermediates products and then to end products using the classical synthesis routes developed for petroleum feedstock. Similarly small molecules (e.g., carboxylic acids) obtained by biomass pyrolysis may, after separation, be converted to chemicals via the existing flow sheets of chemical synthesis. This approach is highly energy demanding and not environmentally sustainable for the production of chemicals since the highly functionalised molecules obtained from biomass are first degraded to C_1 molecules or hydrocarbons which are then be subjected to the traditional chemical synthesis steps in order to be functionalised again.

(ii) *From biomass to products via platform molecules: the biorefinery concept*. A biorefinery is a facility that integrates biomass conversion processes to produce fuels and chemicals. According to the biorefinery scheme described in the Biomass program of the US Department of Energy [1], part of the biomass is converted to fuels via pyrolysis and gasification and the other part is converted by fermentation or chemo-catalytic routes to well-identified platform molecules that can be employed as building blocks in chemical synthesis. A simplified scheme of biorefinery operations is given in Fig. 1.

Table 1
Platform molecules identified by the US DOE [3]

Aspartic acid
Glutamic acid
Levulinic acid
2-Hydroxypropionic acid
2,5-Furan dicarboxylic acid
Glucaric acid
Itaconic acid
1,4-Diacids (succinic, fumaric and malic)
3-Hydroxypropionic acid
Glycerol
Sorbitol
Xylitol/arabitol

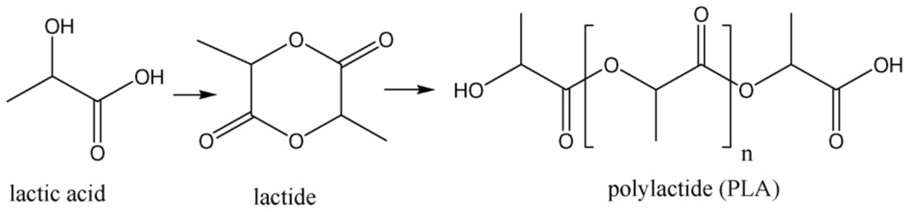
Table 1 gives the 12 platform molecules that have been identified by the US Department of Energy [3] as starting materials to produce chemicals and polymers via catalytic routes. The fermentation processes employed for the production of some of these platform molecules are continuously improved by new genetically modified bacteria or yeasts [4].

Ethanol produced in large amounts (30×10^6 t year^{-1}) by fermentation of starch derivatives and sucrose, can be used both as fuel or fuel precursor, and as building block for chemistry. Lactic (2-hydroxypropionic) acid obtained by fermentation of glucose and polysaccharides is currently used by NatureWorks (Cargill/Dow LLC) to obtain polylactide (PLA), a biodegradable or recyclable polymer, with a potential production of 140,000 t year^{-1} [5] (Scheme 1).

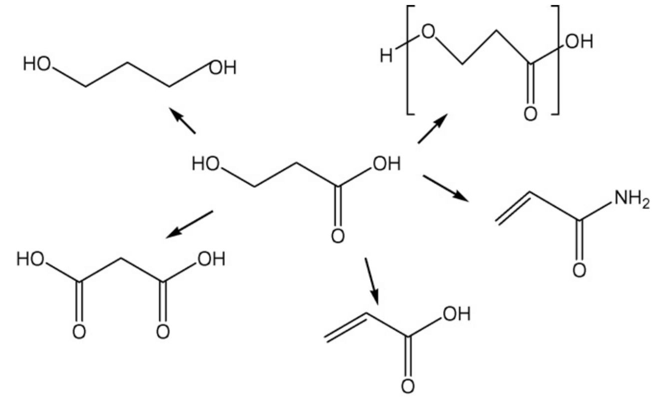
3-Hydroxypropionic acid obtained by fermentation of glucose can also be used as platform molecule to produce various chemicals by catalytic routes [6] (Scheme 2).

Levulinic acid is obtained by hydrolysis of cellulose-containing biomass. R&D is actively conducted at DuPont Co. to employ levulinic acid in the synthesis of pyrrolidones (solvents and surfactants), α-methylene-γ-valerolactone (monomer for the preparation of polymers similar to polymethylmethacrylate), and levulinic acid esters (fuel additives) [7].

(iii) *Direct routes from biomass to products via one-pot reactions*. An attractive way to reduce the processing cost of biomass conversion to valuable products is to decrease the number of reaction steps. This can be done via one-pot reaction possibly associating two or more enzymatic and

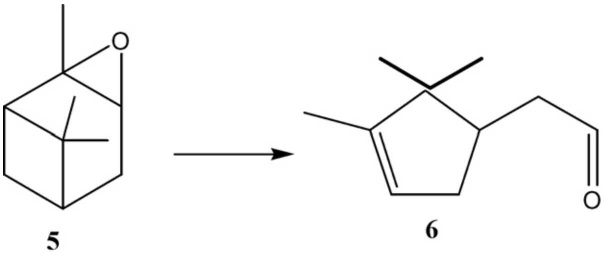


Scheme 1. Synthesis of polylactide (PLA) starting from lactic acid.

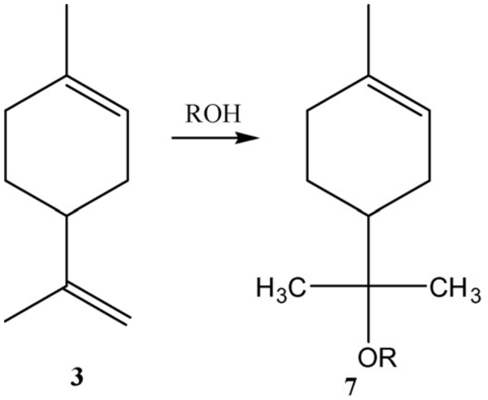


Scheme 2. Synthesis by catalytic routes of various chemicals starting from 3-hydroxypropionic acid.

chemical steps. Examples of cascade catalysis will be given for carbohydrate processing. Also, the formulation of many commercial products (cosmetics, paper, paints, binders, construction materials) often involves a mixture of molecules with the same functionalities (e.g., mixture of diols or polyols). This mixture may well be obtained from biomass via one-pot processes, possibly with different catalytic steps (cascade catalysis), avoiding product isolation thus reducing considerably the processing cost of biomass to chemicals.



Scheme 3. Conversion of α-pinene oxide to campholenic aldehyde.



Scheme 4. Alkoxylation of limonene.

3. Catalytic conversion of terpenes

Heterogeneous catalysis is more and more used for the conversion of terpenes and derivatives in the place of homogeneous processes. The three main starting materials employed in terpene chemistry are α-pinene **1** and β-pinene **2**, which are extracted from turpentine oil (350,000 t year^{-1}) a co-product of paper pulp industry, and limonene **3** extracted from citrus oil (30,000 t year^{-1}). They are used for the synthesis of flavours and fragrances (F&F), although these compounds are often more easily obtained by catalytic routes from hydrocarbons. Thus, citral synthesis requires five steps from α-pinene whereas it is obtained with a 95% yield in the BASF process starting from formaldehyde and isobutene [8] (Fig. 2).

p-Cymene **4**, a precursor of *p*-cresol and various F&Fs, was obtained by dehydrogenation of α-pinene at 300 °C in a continuous fixed-bed flow reactor in the presence of 0.5 wt.% Pd/SiO_2 [9]. Under similar condition, but starting from limonene, *p*-cymene was obtained with a 97% yield and the catalytic activity was stable for 500 h on stream [10]. More interestingly, *p*-cymene was produced under similar reaction conditions with nearly 100% yield from a mixture of di-pentene (Sylvapine DP-378) showing that raw materials need not be purified and still be converted in one step to desired product. [11].

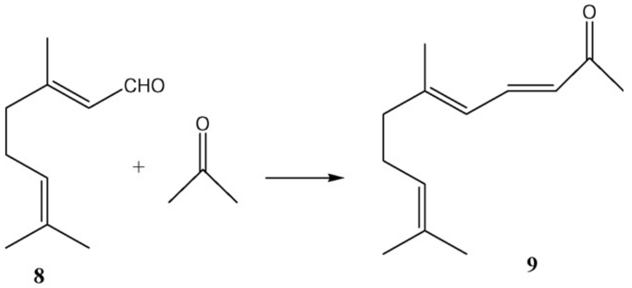
The conversion of α-pinene oxide **5** to campholenic aldehyde **6**, an important intermediate in the synthesis of sandalwood-like fragrances, is traditionally carried out in the presence of $ZnCl_2$ or $ZnBr_2$ salts. Alternative routes have been described using solid catalysts with Lewis acid sites giving high yield of campholenic aldehydes as shown in Table 2 [12–15] (Scheme 3).

The liquid phase alkoxylation of limonene with C_1–C_4 alcohols to 1-methyl-4-[α-alkoxy-isopropyl]-1-cyclohexene **7** was carried out both in batch and continuous fixed-bed reactor at 60 °C on various acidic catalysts [16]. The best yields were obtained in batch (85%) or continuous reactor (81%) using a β-type zeolite with $SiO_2/Al_2O_3 = 25$ (Scheme 4).

Solid basic catalysts can advantageously be used to replace soluble catalysts in the conversion of terpene derivatives. Thus, the aldol condensation of acetone with citral **8** was achieved in the presence of rehydrated hydrotalcite with a 96% yield to a

Table 2
Conversion of α-pinene oxide to campholenic aldehyde on acidic solid catalysts

Catalysts	Reaction conditions	Yield	Refs.
Ti-β zeolite	Vapour phase reaction at 90 °C	94%	[12]
Sulfated alumina	Liquid phase at 0 °C	76%, low deactivation	[13]
Silica-alumina	Liquid phase at 25 °C	72%, no deactivation	[14]
H-US-Y zeolite, HCl-treated	Liquid phase at 0 °C	80%	[15]



Scheme 5. Aldol condensation of acetone with citral.

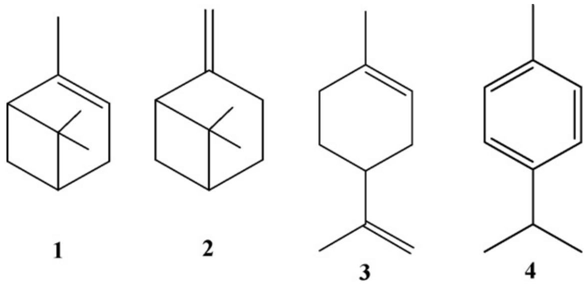


Fig. 2. The main starting materials employed in terpene chemistry.

mixture of *cis*- and *trans*-pseudoionone **9** by operating in liquid phase at 60 °C [17] (Scheme 5).

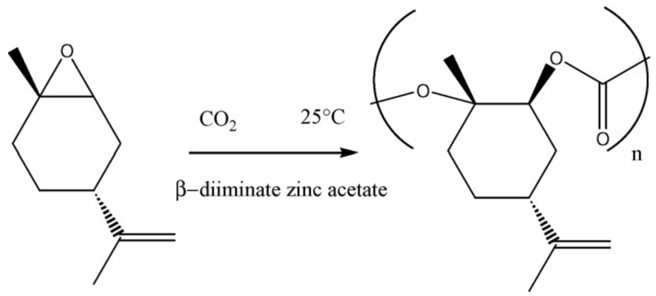
Heterogeneous catalysts are also widely used for selective hydrogenation of terpenes derivatives, e.g., to convert α,β-aldehydes to the corresponding alcohols (cinnamaldehyde to cinnamyl alcohol, citral to geraniol and nerol, etc.), however most of the terpenes derivatives used in flavours and fragrances are not synthesized from natural terpenes.

There are also interesting examples of terpene conversion catalyzed by organometallic complexes. Thus, Byrne et al. [18] have shown that (*R*)-limonene oxide can be copolymerized with CO_2 (also a renewable feedstock!) in the presence of β-diiminate zinc acetate to yield high molecular weight (10 kg mol^{-1}) polycarbonate (Scheme 6).

4. Catalytic conversion of triglycerides

Vegetable oils or triglycerides extracted from the seed of various plants (rapeseed oil, sunflower oil, soybean oil, palm oil, etc.) are a mixture fatty acid esters of glycerol with different chain lengths (C_{12}–C_{18}) and C=C bonds. The content of the different fatty acids is different in the various vegetable oils and can be modified by breeding or genetic modification of crops. There is a serious competition for triglycerides supply between food and feed needs (ca. 100×10^6 t $year^{-1}$), on the one hand, and the growing use for producing bio-fuels and oleochemicals, on the other hand (ca. 15×10^6 t $year^{-1}$).

The scheme given in Fig. 2 summarizes the main catalytic transformations of triglycerides to produce either edible oils and fats or fatty acids, fatty esters, and fatty alcohols employed for the production of oleochemicals. While the hydrogenation steps on metal catalysts are known from a long time and are the subject of continuous improvements in terms of activity, selectivity and stability, the esterification and transesterification reactions catalyzed by acids or bases are still mainly conducted with liquid acids and bases, but the present trend is to develop green processes replacing homogeneous catalysts by solid acid and base catalysts.



Scheme 6. Copolymerization of (*R*)-limonene with carbon dioxide.

Transesterification reactions to produce methyl or ethyl ester of fatty acids (biodiesel) is beyond the scope of this paper which will focus on oleochemicals synthesis yielding surfactants, lubricants and polymers.

4.1. Catalytic conversion of triglycerides to surfactants

The main surfactants and emulsifiers derived from triglycerides are fatty alcohol sulfates, fatty acid esters, alkylglucosides and ethoxylated fatty acid methyl esters. They account for ca. 10^6 t $year^{-1}$, which is a comparatively small amount with respect to surfactants such as alkylbenzene sulfonates produced from petroleum. However, because of their biodegradability and biocompatibility they have a much higher added value and their production is expending, but their development may be hampered by the increasing demand of triglycerides used to produce fatty acid esters used as bio-fuels (Fig. 3).

Fatty acid ester of glycerol are efficient surfactants obtained either by transesterification of triglycerides with glycerol (glycerolysis) or by esterification of fatty acids with glycerol. The challenge in both cases is to obtain selectively glycerol monoesters that are non-ionic surfactants with a good hydrophilic/hydrophobic balance employed in food, cosmetics and pharmaceuticals.

Glycerolysis reactions have been conducted on basic oxides to replace liquid bases. Blancquart et al. [19] have employed various basic oxide (ZnO, MgO, CeO_2, La_2O_3) to catalyze methyl stearate glycerolysis. The selectivity to monoglyceride was rather similar to that obtain with homogeneous catalysts and the nature of the oxide had little effect. Doping MgO with lithium increased the basicity and conversion, but did not change selectivity. Glycerolysis of rapeseed oil on MgO

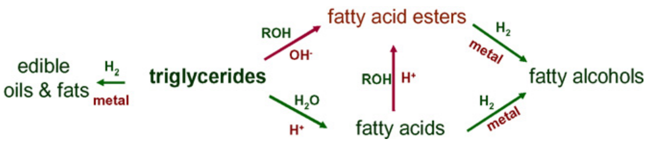


Fig. 3. Scheme of the main catalytic conversions of triglycerides.

Table 3
Solid acid catalysts for the esterification of glycerol and fatty acids [21]

Catalyst	Fatty acid	T (°C)	Time (h)	Yield (%)	Refs.
H-Beta (5 wt.%)[a]	Lauric	100	10	20	[22]
H-USY (5 wt.%)	Oleic	180	5	83	[23]
Amberlyst 31 (7.2 wt.%)	Oleic	90	24	49	[24]
Amberlyst 31 (7.4 wt.%) KA mol sieve (2.2 wt.%)	Oleic	90	24	77	[25]
Amberlyst 15 (1.57 wt.%)	Lauric	110	11.8	44	[26]
H-USY (1.57 wt.%)	Lauric	110	23.5	36	Id
Silicagel-SO_3H (1.57 wt.%)	Lauric	110	8	51	Id
HMS-SO_3H (1.57 wt.%)	Lauric	110	10	52	Id
MCM41-SO_3H (1.57 wt.%)	Lauric	110	24	53	Id
MCM41-SO_3H (5 wt.%) end-capped	Lauric	100	24	60	[27]
MCM41-SO_3H (5 wt.%) MPMDS	Lauric	100	10	60	[28]

[a] wt.% of catalyst with respect to the total weight of reaction medium.

catalysts gave a 63% yield to monoglyceride [20]. The preparation of glycerol monoester by esterification of fatty acid with glycerol was achieved with acidic solids to substitute sulfuric acid [21–28]. Table 3 gives the yields of glycerol monoesters obtained by esterification of lauric and oleic acids with glycerol on solid acids.

Fatty acid esters of sugars are also very important biodegradable and biocompatible surfactants that are prepared either by transesterification of methyl ester with sugar on basic catalysts or by esterification of fatty acids with sugar on acidic catalysts. Liquid acids and bases have been replaced by enzymatic catalysis with lipase giving a higher yield to monoester [29,30], but solid catalysts have not been used extensively so far.

Alkylglucosides are a class of valuable commercial surfactants particularly for cosmetics applications because of their bio-compatibility. They are obtained by acetalization of carbohydrates with fatty alcohols in the presence of acid catalysts. Glucose acetalization gives a mixture of products with glucofuranoside or glucopyranoside rings and various amounts of oligomers as shown in Scheme 7.

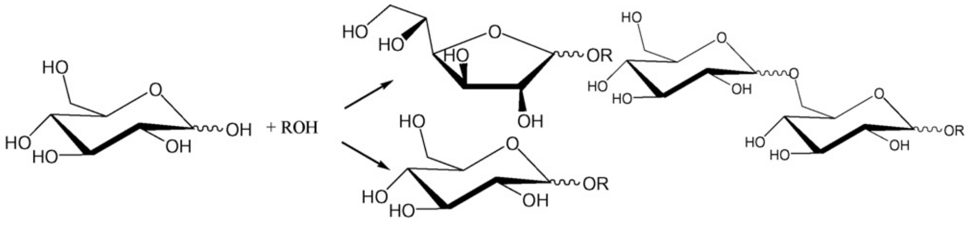
Zeolites and MCM-41 have been used as acidic catalysts to achieve the acetalization of glucose with alcohols of different chain lengths [31,32]. It was shown that shape selectivity effects decrease the amount of oligomers formed and that activity and selectivity can be controlled with the Si/Al ratio. In the glucosidation of n-butanol at 393 K the furanoside/pyranoside ratio increased from 2.5 to 6 as the pore diameter of MCM-41 decreased from 5.3 to 2.5 nm because of the lower diffusivity of the more bulky pyranoside ring in small pores. The kinetics and selectivity of glycosylation between glucose and n-butanol has been investigated in details over various dealuminated HY zeolites by Chapat et al. [33].

Fatty alcohols are obtained by hydrogenation of fatty acids or fatty acid esters in the presence of metal catalysts. The selective reduction of unsaturated esters to unsaturated alcohols is particularly difficult to achieve. The selective hydrogenation of methyl oleate to the corresponding unsaturated alcohol was achieved with Ru–Sn–B/Al_2O_3 catalysts prepared by reduction with $NaBH_4$ of Ru and Sn salts co-impregnated on alumina [34].

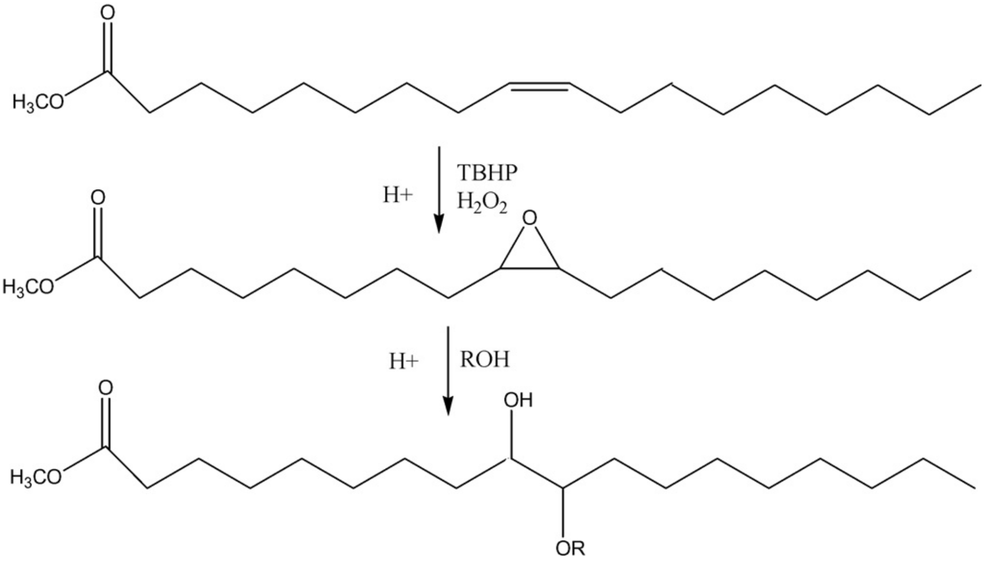
4.2. Catalytic conversion of triglycerides to lubricants

Because almost 50% of lubricants leak and spread out in the environment, there is a need for biodegradable lubricants produced from renewables. Fatty acid esters could be suitable lubricants, but their resistance to oxidation and tribological properties need to be improved. This can be achieved by epoxidation of the fatty acids followed by alcoholysis of the epoxide.

The epoxidation of fatty acid methyl esters (FAME) is traditionally conducted in strong acidic media, e.g., with peracetic acid in sulfuric acid solutions. It has been shown that these reactions can be conducted by environmentally benign route in the presence of acidic solids. Thus, the epoxidation of a mixture of FAME from sunflower oil were epoxided by *tert*-butylhydroperoxide (TBHP) at 363 K in the presence of Ti-MCM-41 catalysts yielding 98% conversion with 85% selectivity to mono-epoxy compounds [35]. Ti/SiO_2 (aerosil) catalysts showed comparable activity and selectivity indicating that the presence of ordered mesoporous framework is not necessary. In the same way Rios et al. [36] used different Ti-MCM-41 materials with pores diameters ranging from 1.9 to 4.1 nm and amorphous Ti/SiO_2 catalysts with different Ti-dispersion to perform methyl oleate epoxidation with TBHP at 70 °C. Selectivities higher than 95% were obtained whatever the structure of the supporting



Scheme 7. Glucose acetalization.



Scheme 8. Epoxidation of fatty acid esters followed by alcoholysis of the epoxide.

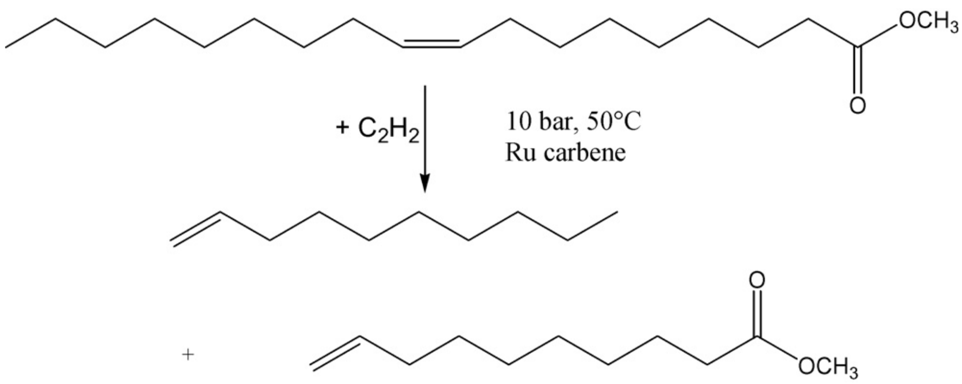
material provided titanium is well dispersed. It was shown that no leaching occurs and that catalysts can be recycled (Scheme 8).

The alcoholysis with different alcohols of epoxidized FAME was studied on acidic resins of various structure and acid strength [37,38]. The addition of methanol on epoxidized methyl oleate at 60 °C in the presence of Nafion entrapped in silica (SAC13) or of Amberlyst 15, a sulfonated styrene-divinylbenzene copolymer, resulted in complete conversion with selectivity higher than 98%, but the reaction rate was higher on the more acidic SAC13 catalyst (60 s^{-1}) than on Amberlyst 15 (2.4 s^{-1}). On the other hand a too strong acidity was detrimental to selectivity in the case of branched alcohols such as neopentanol. The viscosity index of final products was improved, e.g., from 4.5 $mm^2 s^{-1}$ for methyl oleate to 30.3 $mm^2 s^{-1}$ for hydroxy-neopentoxy methyl stearate obtained by addition of neopentanol on the epoxidized methyl oleate, while their biodegradability was maintained.

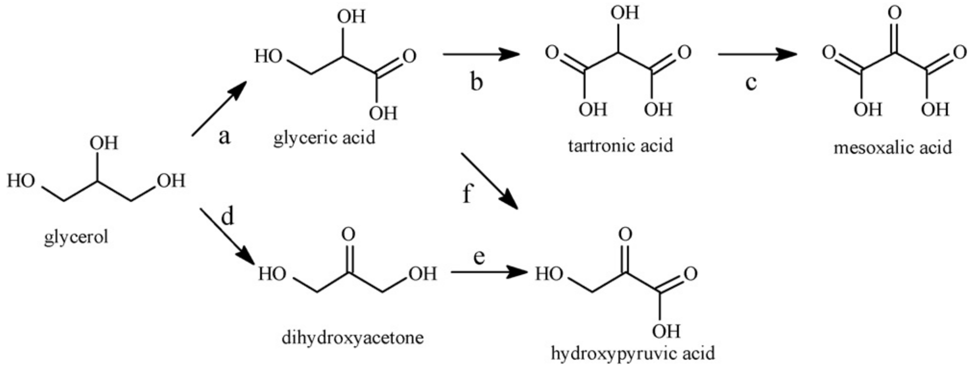
4.3. *Catalytic conversion of triglycerides to polymers*

Catalytic reactions involving C=C bonds are widely used for the conversion of unsaturated fatty compounds to prepare useful monomers for polymer synthesis. Heterogeneous catalysis played a modest role so far in the production of monomers for polymer manufacture. Interestingly dimerization of fatty acids by on montmorillonite clays at 250 °C results in diacids that can be hydrogenated to diols. These diacids and diols can be employed to produce polyesters, polyethers, polyamides, and polyurethanes. Polyethers from dimer diols are valuable for the production of highly hydrophobic polymers stable in acidic media [39]. The epoxidation of triglycerides followed by ring opening results in the formation of OH groups along the fatty acid chains yields useful materials for the manufacture of polyurethanes [40].

Homogeneous catalysis has been widely used to prepare monomers. Catalytic C–C coupling reactions of unsaturated fatty compounds have been reviewed by Biermann and Metzger [41]. Hydroformylation reaction of soybean and linseed oils catalyzed by rhodium complexes gave polyaldehydes in quantitative yield [42]. Metathesis reactions involving unsaturated fatty compounds to prepare ω-unsaturated fatty acid esters were applied by Warwel et al. [43]. Thus the ethenolysis of methyl oleate catalyzed by ruthenium carbenes developed by Grubb yields 1-decene and methyl-9-decenoate, which can be very useful to prepare monomers for polyolefins, polyesters, polyethers and polyamides (Scheme 9).



Scheme 9. Ethenolysis of methyl oleate.



Scheme 10. Selective oxidation of glycerol.

5. Catalytic conversion of glycerol

Glycerol can be considered as a renewable feedstock in so far as it is the co-product of triglyceride saponification or of transesterification with methanol or ethanol to prepare fatty acid esters employed as bio-diesel. Glycerol should find new outlets to optimise the economy of biodiesel production and to rebalance supply and demand [44]. As far as chemicals are concerned, the production of glycerol esters (see previous section) employed as emulsifiers, surfactants and lubricants is one of the main glycerol outlet. Transformation by oxidation, dehydration and dehydroxylation described in the following sections are also interesting routes to valuable products.

5.1. *Oxidation of glycerol to C_3 oxygenates*

The selective oxidation of glycerol leads to various valuable oxygenates depicted in the following figure. Most of these compounds are currently prepared by enzymatic reactions and have a small market because of their high price. Besson and Gallezot [45] have shown that they can be obtained by oxidation with air of aqueous solutions of glycerol in the presence of carbon-supported platinum and palladium catalysts. The selectivity can be tuned by promotion of the noble metals with bismuth or by operating under controlled pH (Scheme 10).

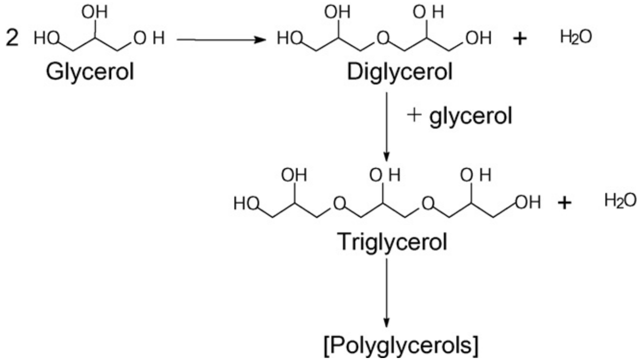
Garcia et al. [46] found that the oxidation of glycerol at basic pH on palladium and platinum catalysts yielded 70% glycerate. Using bismuth-promoted platinum under similar reaction conditions, the oxidation leads to dihydroxyacetone with a 25% yield. Fordham et al. [47] found that glyceric acid oxidation 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. Abbadi and Van Bekkum [48] obtained a 93% selectivity to hydroxypyruvic acid at 95% conversion of glyceric acid on 5% Bi–5% Pt/C catalyst without pH regulation. Fordham et al. [49] have studied the preparation of mesoxalic acid by oxidation of sodium tartronate on PtBi/C catalyst at 60 °C without pH control; the maximum yield was 65% at 80% conversion. A total conversion of tartronic acid was obtained at 80 °C giving 50% yield of mesoxalic acid with no other products, because all by-products were totally oxidized into CO_2.

More recently the oxidation of glycerol was conducted in the presence of gold catalysts in basic medium [50,51]. Glycerol was oxidized with oxygen at 60 °C with a selectivity of 100% at 56% conversion on 1 wt.% Au/activated carbon. Graphite supported catalysts gave comparable results. The selectivity of glycerol oxidation on gold catalysts on various supports was shown to depend critically upon the size of gold particles [52].

5.2. *Conversion of glycerol to polyglycerols and derivatives*

Polyglycerols obtained by dehydration of glycerol are employed as surfactants, lubricants, cosmetic, food additives, etc. Their esterification with fatty acids leads also to valuable emulsifiers or metal working fluids. There are three challenges in the etherification of glycerol, viz.: (i) replace liquid bases by solid catalysts to achieve a greener and more efficient process; (ii) control the chain length to obtain a suitable hydrophilic-lipophilic balance in PGEs; (iii) avoid the formation of acrolein by internal dehydration. The etherification of glycerol by dehydration in the presence of liquid bases leads to a mixture of dimers, trimers and cyclic or branched oligomers (Scheme 11).

Zeolites have been used to take advantage of shape selectivity effect to minimize oligomer formation as described



Scheme 11. Synthesis of polyglycerols through intermolecular dehydration of glycerol.

Table 4
Glycerol dehydration

Catalysts	Diglycerol (%)	Triglycerol (%)	Refs.
A-zeolite	32	25	[53]
β-Zeolite	36	18	[54]
Cs-ZSM-5	94	6	[55]
Cesium-impregnated MCM-41	60	17	[56]

Selectivity to di- and triglycerol.

in two patents [53,54] (Table 4). The selectivity to monoglycerol was improved over Cs-ZSM-5 catalyst but the activity was too low [55]. A fair compromise between activity and selectivity was obtained by Clacens et al. [56] using cesium-impregnated mesoporous MCM-41 (Table 4).

5.3. Hydrogenolysis of glycerol to 1,2- and 1,3-propanediol

Glycerol can be selectively dehydroxylated either to 1,2-propanediol (1,2-PDO), a chemical that can advantageously replace ethylene glycol as anti-freezing agent or to 1,3-propanediol (1,3-PDO), which copolymerized with terephtalic acid, give polyesters with unique mechanical properties. 1,3-PDO is currently produced by catalytic routes from ethylene oxide (Shell route) or acrolein (Degussa-DuPont route). The microbial production of 1,3-PDO is under development by DuPont-Genencor to produce 1,3-PDO from glucose [57] (Scheme 12).

Chaminand et al. [58] 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. Different catalysts (Cu, Pd, Rh), supports (ZnO, C, Al_2O_3), solvents (H_2O, sulfolane, dioxane), and additives (H_2WO_4) were tested to improve reaction rate and selectivity. The best selectivity (100%) to 1,2-PDO was obtained by hydrogenolysis of water solution of glycerol in the presence of CuO/ZnO catalysts. To control the selectivity toward 1,3-PDO the reaction was conducted with rhodium catalysts with tungstic acid added to the reaction medium. The best selectivity to 1,3-PDO (1,3-PDO/1,2-PDO = 2) was obtained by operating in sulfolane. The presence of iron dissolved in the reaction medium was also beneficial for the selectivity to 1,3-PDO. A mechanism was proposed to account for the effect of the different reaction parameters.

6. Catalytic conversion of carbohydrates

Carbohydrates are the main source of renewables employed for the production of bio-based products. Sucrose (total production130 × 10^6 t $year^{-1}$) and starch (40 × 10^6 t $year^{-1}$ used in industry), are the two major sources, 50% of the latter being used for industrial purpose. Polysaccharides such as inulin are gaining importance as a source of fructose. Two carbohydrates of animal origin, lactose and chitin are of commercial importance. Reviews on carbohydrates employed as raw materials for the chemical industry has been given by van Bekkum and Besemer [59] and by Lichtenthaler and Peters [60].

6.1. One-pot reaction: cascade catalysis

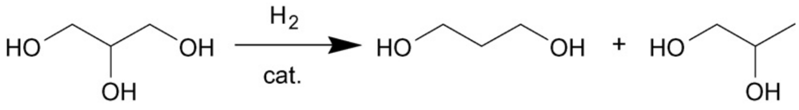
Multistep reactions carried out by cascade catalysis without intermediate product recovery decrease operating time and may reduce considerably the amount of waste produced. Thus, It has been shown that sorbitol can be obtained in one-pot reaction from starch-derived polysaccharides using ruthenium supported on acidic Y-zeolite. The acidic sites of the zeolite catalyse the polysaccharide hydrolysis yielding transiently glucose, which is hydrogenated to sorbitol on ruthenium [61]. Thus, a solution of corn starch (25%) was hydrogenated to a mixture of sorbitol (96%), mannitol (1%), and xylitol (2%).

Similarly a one-pot process for hydrolysis and hydrogenation of inulin to sorbitol and mannitol was achieved with Ru/C catalysts. The hydrolysis was catalyzed by the carbon support onto which acidity was introduced by pre-oxidation with ammonium persulfate [62]. The hydrolysis of long inulin chains was faster than short chains due to multi site attack and a stronger adsorption of long chains on the carbon surface.

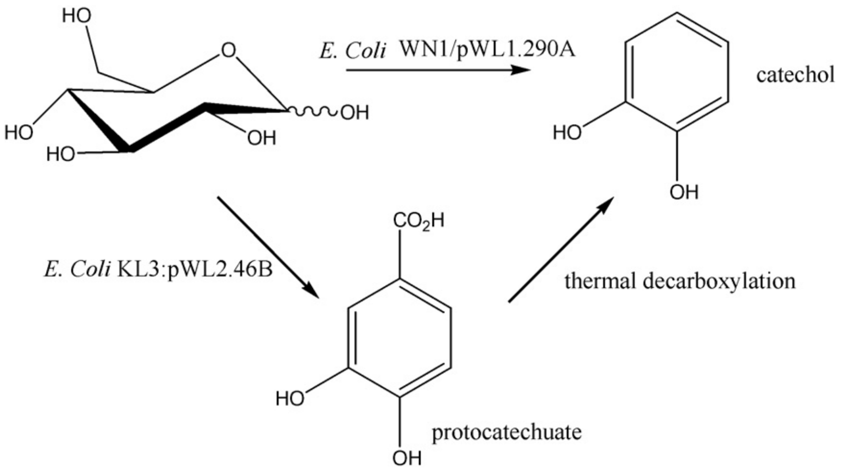
2,5-Furanedicarboxylic acid, a potential substitute for terephtalic acid is obtained from fructose in two-step process: dehydration to 5-hydroxymethylfurfural catalyzed by liquid or solid acids, which is subsequently oxidized to 2,5-furanedicarboxylic acid (see Section 6.6 on furan chemistry). Instead, Ribeiro and Schuchardt [63] succeeded in converting fructose to 2,5-furanedicarboxylic acid with 99% selectivity at 72% conversion in one-pot reaction over a bifunctional acidic and redox catalyst consisting of cobalt acetylacetonate encapsulated in sol–gel silica.

In the three former examples, the reactions steps took place on heterogeneous catalysts. However, cascade catalysis without recovery of intermediate products may involve enzymatic catalysis, homogeneous catalysis and heterogeneous catalysis. Combination of enzymatic and chemical steps can give a better yield. Thus Frost [64] has shown that direct enzymatic conversion of glucose to catechol is limited to 5% yield because of the poisoning of the strain by the aromatic molecule. Instead a 43% yield to catechol was obtained by combining enzymatic and decarboxylation steps as shown in Scheme 13.

Various examples of one-pot reactions combining enzymatic and chemo-catalytic steps were given by Bruggink et al [65,66]. One of the most representative example consists of a four-steps



Scheme 12. Selective dehydroxylation of glycerol.



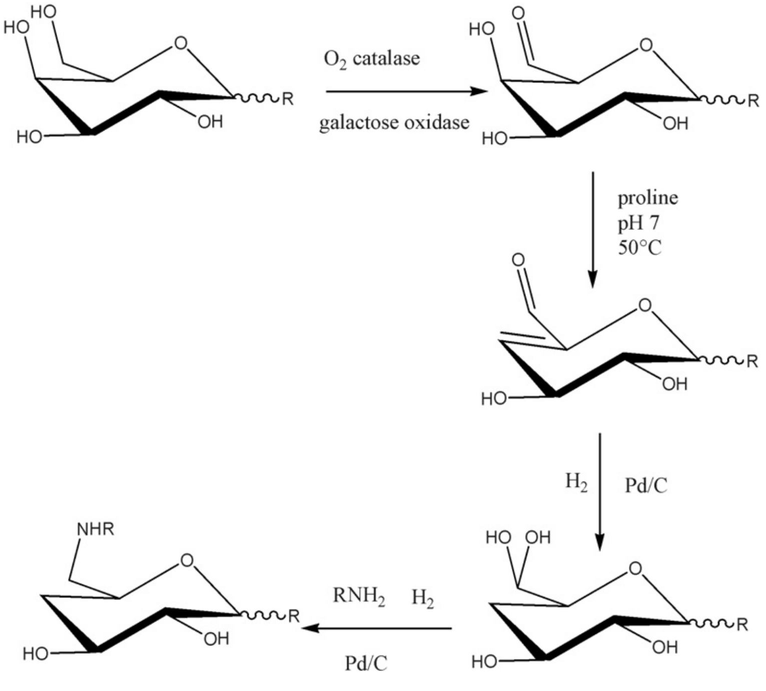
Scheme 13. Conversion of glucose to catechol through enzymatic conversion or a combination of enzymatic and chemical steps.

conversion of glucoside to aminodeoxysugar without intermediate product recovery as described in Scheme 14.

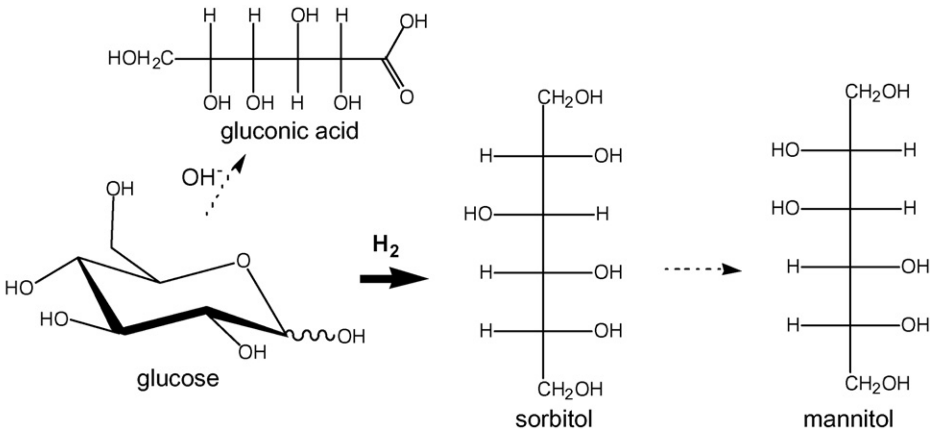
6.2. Hydrogenation of glucose and derivatives

Glucose issued from starch or sucrose hydrolysis is hydrogenated to sorbitol (ca. 800,000 t year^{-1}) a commodity product used in food, pharmaceutical and chemical industries as well as an additive in many end-products. The main by-products of the reaction are gluconic acid formed by the Cannizaro reaction and mannitol formed by sorbitol epimerization (Scheme 15).

Catalysts allowing a 100% conversion and 99% selectivity are required. Also, they should be stable after many recycling operations or for extended period of time on stream in continuous reactor. Most of the industrial production is still conducted batch-wise on Raney nickel catalysts promoted with electropositive metal atoms such as molybdenum and chromium [67], but, because of the risk of nickel or metallic promoter leaching, they tend to be replaced by carbon-supported ruthenium catalysts which are also more active. However, active carbon powders are difficult to handle and recycle in batch operation, therefore a continuous process with formed carbon support are desirable. Nicolaus et al [68] prepared 1.8% Ru/C catalyst by cationic exchange or anionic adsorption on 0.8 mm Norit extrudates. These catalyst used in continuous trickle-bed reactor provided up to 99.5% yield in sorbitol for up to 596 h on stream. No leaching of ruthenium was detected. The activity at low conversion (initial activity) was 1080 mmol h^{-1} g$_{\mathrm{Ru}}^{-1}$ compared to 50 mmol h^{-1} g$_{\mathrm{Ni}}^{-1}$ on 48% Ni/kieselguhr catalyst. Glucose hydrogenation was also conducted on Ru–Pt/C bimetallic catalysts prepared by co-exchange of Pt and Ru amino cations. Interestingly, the activity



Scheme 14. Four-step conversion of glucoside to aminodeoxysugar.



Scheme 15. Hydrogenation of glucose.

passed through a maximum at 1470 mmol h^{-1} g_{Ru}^{-1} for the specific atomic composition $Ru_{56}Pt_{44}$. Pt–Ru catalysts were also more selective to sorbitol because the rate of epimerization to mannitol decreased. The contact time with the catalyst can be increased without loss of selectivity thus allowing operation at total conversion of glucose and at more than 99% selectivity over a large domain of liquid flow rate. The bimetallic catalysts loaded in trickle-bed reactor yielded 2 t/(day kg_{Ru}) of sorbitol at 99.5% purity. Platinum alloying extends the catalyst stability because it may prevent the formation of oligomeric or cracking products and also prevent any oxidation of ruthenium.

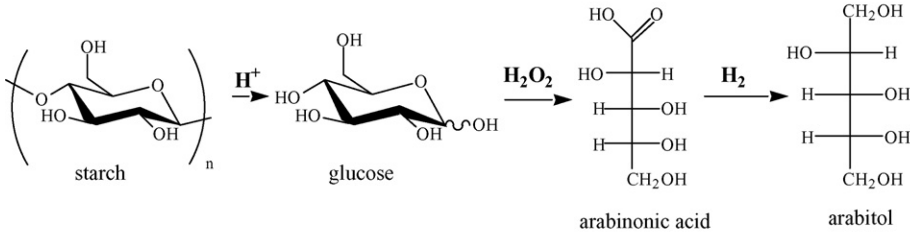
Hydrogenation of glucose to sorbitol was achieved on ruthenium catalysts supported on activated carbon cloths (ACC) obtained by carbonization and CO_2 activation of woven rayon [69]. Catalyst 0.9 wt.% Ru/ACC was loaded with ruthenium by cationic exchange or anionic adsorption both giving an homogeneous distribution of 2 nm ruthenium particles in carbon fibers. The ACC was clamped on a support fitting along the autoclave walls thus allowing an easy recycling of the catalyst since, unlike catalysts in powder form, no filtration are required and there is no attrition or leaching. Glucose hydrogenation was achieved with a 99.5% selectivity to sorbitol at 99.7% conversion with an activity of 2.4 mol h^{-1} g_{Ru}^{-1} comparable to Ru-catalyst in powder form. The hydrogenation of glucosone to fructose was achieved on 2.5% Pd/ACC at a rate of 0.5 mol h^{-1} g_{Pd}^{-1}.

There is a great interest to convert C_6 carbohydrates available in large supply from starch or sucrose into C_5 and C_4 polyols that are little present in biomass and find many applications in food and non-food products. Thus, glucose can be converted to arabitol by an oxidative decarboxylation of glucose to arabinonic acid followed by hydrogenation to arabitol (Scheme 16).

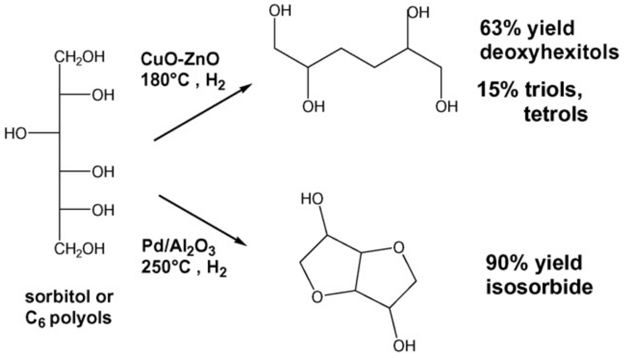
The main pitfall is to avoid dehydroxylation reactions leading to deoxy-products not compatible with the purity specifications required for arabitol. Aqueous solutions (20 wt.%) of arabinonic acid were hydrogenated on Ru-catalysts in batch reactor [70]. The selectivity was enhanced by adding small amounts of anthraquinone-2-sulfonate (A2S), which decreased the formation of deoxy by-products. Thus, by adding 260 ppm of A2S with respect to arabinonic acid the selectivity to deoxy-products decreased from 4.2 to 1.6%. A2S acted as permanent surface modifier since the catalyst was recycled with the same selectivity without further addition of A2S. The highest selectivity to arabitol was 98.9% at 98% conversion with a reaction rate of 73 mmol h^{-1} g_{Ru}^{-1} at 80°.

6.3. Dehydroxylation of carbohydrates

Deoxyhexitols consisting of C_6 diols, triols, and tetrols are well suited to replace polyols derived from petrochemistry for applications in polyester and polyurethane manufacture. Comparatively few investigations on catalytic hydrogenolysis of carbohydrates were performed [71,72] and most of them were designed to produce C_2–C_3 polyols, particularly glycerol, rather than higher molecular weight polyols. Sorbitol was taken as model molecule to study the hydrogenolysis to C_4–C_6 products [73]. To improve the selectivity to deoxyhexitols, catalysts and reaction temperature were optimised to favor the rupture of C–OH bonds (dehydroxylation reactions) rather than C–C bond rupture. Copper-based catalysts, which have a low activity for hydrogenolysis of C–C bonds, were employed to



Scheme 16. Oxidative decarboxylation of glucose.



Scheme 17. Hydrogenolysis of sorbitol to C_6 polyols.

treat 20 wt.% aqueous sorbitol solutions in the temperature range of 180–240 °C. 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 (Scheme 17).

In contrast, operating in the presence of palladium catalysts at 250 °C under 80 bar of hydrogen pressure, cyclodehydration reactions of sorbitol and mannitol occurred with formation of cyclic ethers: isosorbide, 2,5-anhydromannitol, 2,5-anhydroiditol, and 1,4-anhydrosorbitol [74]. Up to 50% and 90% yield to isosorbide were obtained from sorbitol and mannitol, respectively. These mixtures of polyols were effectively employed to synthesize alkyd resins and make decorative paints which performed comparable to the commercial ones.

6.4. *Catalytic oxidation of mono- and di-saccharides*

Oxidation reactions are widely used for upgrading carbohydrates to a varieties of high added value chemicals used in detergents or pharmaceuticals (Vitamin C). Enzymatic and microbial oxidation reactions are widely used for that purpose, but homogeneous catalysis is also widely used. Thus, oxidation with hypochlorite mediated by TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) has been generalized to a large number of carbohydrates [75]. To replace the non-green hypochlorite agent by oxygen the catalytic system was improved by adding co-catalysts such as laccase enzyme and the catalytic system was immobilized [76] The catalytic system $RuCl_2(PPh_3)_3$/TEMPO was also used to replace hypochlorite by oxygen [77]. Oxidation reactions with H_2O_2 mediated by metal phthalocyanine catalysts have also proved very efficient to oxidize various carbohydrates including the oxidation of insoluble substrates such as native starch [78]. Carbohydrate oxidation reactions with oxygen catalyzed by supported metals underwent a considerable development in the 1990s following pioneering works in the early 1970s [79]. The oxidation of carbohydrates on metal catalysts have been reviewed by Besson and Gallezot [80,81].

Glucose oxidation to gluconic acid, a biodegradable chelating agent and an intermediate in food and pharmaceutical industry, was achieved with air oxidation in the presence of palladium catalysts. Unpromoted palladium catalysts were active in glucose oxidation, but the rate of reaction was low because of the over-oxidation of Pd-surface, and side oxidation reactions decreased the selectivity. Using Pd–Bi/C catalysts (5 wt.% Pd, Bi/Pd = 0.1) prepared by deposition of bismuth on the surface of 1–2 nm palladium particles, the rate of glucose oxidation to gluconate was 20 times higher and the selectivity at near total conversion was high on the fresh and recycled catalysts [82] (Table 5). Bismuth was assumed to act as a co-catalyst protecting palladium from over-oxidation because of its stronger affinity for oxygen. The metal-catalyzed oxidation gave comparable selectivity and higher productivity than enzymatic glucose oxidation.

Glucose oxidation has been conducted in the presence of gold catalysts [83–85] showing that gold catalysts are indeed active for oxidation with oxygen at basic pH, however, the activity was strongly dependent on particle size and the selectivity much lower than those reported on Pd–Bi catalysts [82]. Precise data on specific activity, selectivity and stability of catalysts should be assessed to make valid comparison with former data on Pd-Bi catalysts.

Gluconate **1** could be oxidized with oxygen on Pt-catalysts into glucarate **2** or 2-keto-D-gluconate **3**, the latter being a valuable intermediate (Fig. 4). Besson et al. [86] conducted the reaction at basic pH, but the yield to 2-ketogluconate was limited by the formation of degradation products. Abbadi and van Bekkum [87] reinvestigated this reaction on 5% Bi/5% Pt/C catalyst without regulating the pH. The oxidation reaction proceeded almost to completion giving 98% selectivity to the desired product.

Table 5
Product distribution in glucose oxidation on bismuth-promoted palladium [82]

Catalyst[a] (run)	Conversion[b] (%)	Yield (mol%)				Selectivity (%)
		1	**2**	**3**	**4**	
PdBi/C (1st)	99.6	99.4	<0.4	<0.4	0.2	99.8
PdBi/C (2nd)	99.7	98.9	<0.4	0.6	0.2	99.1
PdBi/C (3rd)	99.8	98.5	0.4	0.8	0.2	98.7
PdBi/C (4th)	99.9	98.5	0.4	0.7	0.2	98.6
PdBi/C (5th)	99.9	99.1	<0.4	0.6	0.2	99.2
Pd/C	82.6	78.1	1.4	2.3	0.7	94.6

1, gluconate; **2**, 2-ketogluconate; **3**, 5-ketogluconate + glucarate; **4**, fructose. Reaction conditions: 1.7 mol L^{-1}, $T = 313$ K, pH 9; [glucose]/[Pd] = 787; air at atmospheric pressure.

[a] 4.7 wt.% Pd; Bi/Pd = 0.1.

[b] After 155 min on PdBi/C and 24 h for Pd/C.

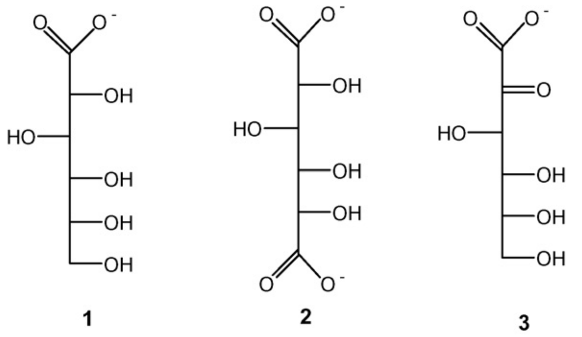


Fig. 4. Schematic representation of gluconate, glucarate and 2-keto-D-gluconate.

Abbadi et al. [88] have studied the oxidation of lactose, a co-product of milk industry, on PtBi/C catalyst at pH 7. Lactobionate was formed transiently and subsequently converted to 2-keto-lactobionate with a final yield of ca. 80%. Starting from lactobionate without pH control, 2-keto-lactobionate was obtained with 95% selectivity, but the oxidation reaction stopped at 50% conversion due to the poisoning of Pt–Bi/C catalysts (Scheme 18).

The oxidation of L-sorbose to 2-keto-L-gulonic acid, an important intermediate in the synthesis of Vitamin C, was extensively studied by Baiker and co-workers [89–91]. Pt/Al_2O_3 catalyst, promoted or not with bismuth, gave a poor yield. By adsorbing hexamethylenetetramine (HMTA) on the surface of Pt/C catalyst (HMTA/Pt_s mol/mol = 0.1), the selectivity increased from 51 to 95% at 30% conversion. Selectivity was also improved (66% at 50% conversion) upon addition of trace amounts of tributylphosphine, but the improvement was lower than with amines.

Verraest et al. [92] investigated the catalytic oxidation of methylfructofuranoside and of inulin. The aim was to prepare polycarboxylates that could be used in detergents because of their sequestering properties for calcium. Methylfructofuranoside was oxidized at the C_6 position with 83% selectivity at 100% conversion by conducting the reaction at 60 °C on a 5% Pt/C catalyst at pH 9. The oxidation of inulin conducted under the same conditions, resulted in the oxidation of only a fraction of the primary alcohol functions and a lower selectivity (typically 65% selectivity at 25% conversion). The longer the chain length, the lower the fraction of oxidized functionalities. This was attributed to the steric hindrance of the catalyst surface by the bulky reactant intermediate, and/or to the low affinity of the polycarboxylates already formed for the platinum surface.

6.5. Catalytic conversion of polysaccharides

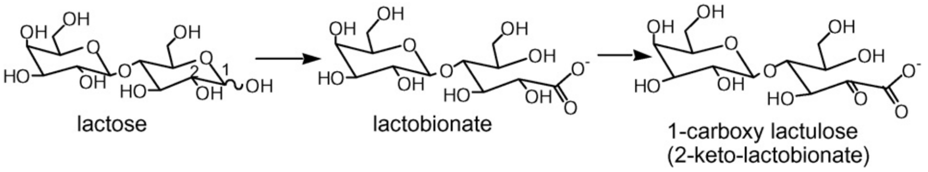
Polysaccharides are widely available renewable polymers but it is difficult to find cost effective process to convert them to valuable end-products. Due to its large availability and low cost, native starch has been used for a long time in the preparation of different end-products. To obtain specific properties, native starch has to be chemically or enzymatically modified. Because, native starch is an insoluble, partially crystallized solid polymer, chemical modifications are difficult to achieve and require the use of soluble catalysts. To meet specific hydrophilic properties native starch has been either modified by oxidation [93–95] or by grafting hydrocarbon chains [93,96].

Hydrophilic starch obtained by partial oxidation is widely used in paper and textile industries and can be potentially applied in a variety of applications, e.g., for the preparation of paints, cosmetics, and superabsorbents. The oxidation occurs at the C_6 primary hydroxyl group or at the vicinal diols on C_2 and C_3 involving a cleavage of the C_2–C_3 bond to give carbonyl and carboxyl functions (Scheme 19).

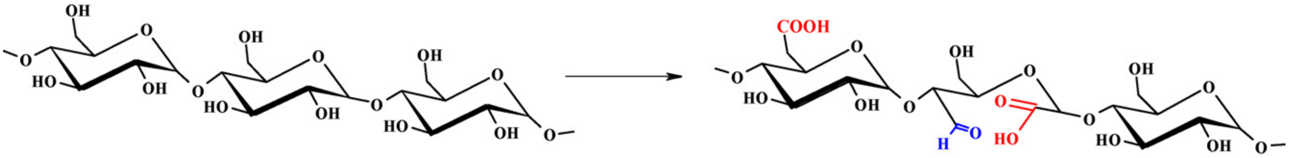
Several transition metal catalysts based on Fe, Cu or W salts (0.01–0.1 mol%) have been proposed to activate H_2O_2, which is a well-suited oxidant from an environmental and economical point of view. However, the concentration of metal ions was quite high and heavy metals were retained by the carboxyl functions of oxidized starch, which has good complexing properties.

Efficient catalytic methods for native starch oxidation with H_2O_2 in the presence of iron tetrasulfophthalocyanine (FePcS) were proposed [94]. Starches from different origin (potatoes, rice, wheat, corn) were oxidized by H_2O_2 following two operating modes.

Oxidation of starch aqueous suspension in the presence of iron phthalocyanine gives both carboxylic and carbonyl groups



Scheme 18. Oxidation of lactose.



Scheme 19. Hydrophilic starch obtained by partial oxidation.

Table 6
Oxidation of starch in aqueous suspension with H_2O_2 in the presence of iron phthalocyanine; effect of substrate/catalyst ratio

AGU/Fe	DS_{COOH}[a]	$DS_{C=O}$[a]
25800:1	0.70	3.20
12900:1	2.00	10.40
6450:1	2.00	9.00

Reaction conditions: 58 °C; pH 7; reaction time, 7 h; molar ratio H_2O_2:AGU, 1:2.1.

[a] Degree of substitution expressed per 100 anhydroglucose units (AGU).

as shown in Table 6. The best yields were obtained with a molar ratio 12,900/1 (0.0078 mol%), but the oxidation was still quite efficient with 0.0039 mol% of catalyst (25,800/1 AGU/catalyst ratio). The very small amount of catalyst needed for successful oxidation of starch represents a very important advantage with respect to oxidation methods based on metal salts that need at least 0.2 mol% [12]. Starch oxidized in the presence of $FeSO_4$ retains significant amounts of residual iron whereas starch obtained with FePcS catalyst exhibits practically the same final Fe-content as the starting potato starch. High metal content prevents the use of oxidized starch in applications where brightness and/or low metal content are required.

The oxidation of native starch by incipient wetness method consist of 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 25,800/1 the oxidation of potato starch by the incipient wetness method was efficient providing 1.5 carboxyl and 5.6 carbonyl functions per 100 AGU. This 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). This catalytic system was very flexible because by simple modifications of the reaction conditions it was possible to prepare oxidized starches with the desired level of carboxyl and carbonyl functions that are suitable for different applications. No wastes were formed because the process did not involve any acids, bases or buffer solutions. Hydrophilic starch was incorporated successfully in paint and cosmetic formulations.

To prepare more hydrophobic starches for specific applications, partial substitution of starch with acetate, hydroxypropyl, alkylsiliconate or fatty-acid ester groups were described in the literature. An alternative route was employed consisting of grafting octadienyl chains by butadiene telomerization [93,96]. The reaction was catalyzed by hydrosoluble palladium-catalytic systems prepared from palladium diacetate and trisodium tris(*m*-sulfonatophenyl)phosphine (TPPTS). Starch octadienyl ethers are expected to be much less sensitive towards hydrolysis compared to the esterified starches (Scheme 20).

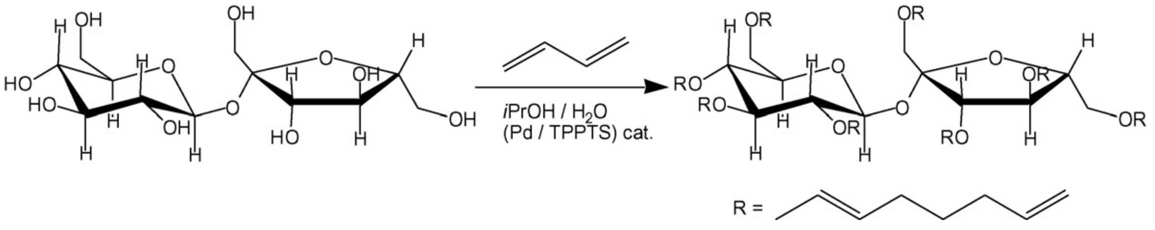
The reaction was first conducted with success on sucrose [97]. The degree of substitution (DS) obtained was controlled by the reaction time. Thus under standard conditions (0.05% $Pd(OAc)_2$/TPPTS, NaOH (1N)/iPrOH (5/1), 50 °C) the DS was 0.5 and 5 after 14 and 64 h reaction time, respectively. The octadienyl chains were hydrogenated quantitatively in the presence of 0.8 wt.% $[RhCl(TPPTS)_3]$ catalyst in H_2O/EtOH (50/10) mixture yielding a very good biodegradable surfactant (surface tension of 25 $mN\,m^{-1}$ at 0.005% concentration in water) [98].

The transposition of this reaction to starch was challenging because this substrate is insoluble in water at room temperature 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, also for obvious economical reason the catalyst/starch ratio should be kept low. Fig. 5 shows that at 90 °C, with 0.5 wt.% of $Pd(OAc)_2$, the DS reached almost 0.6 while less than 0.3 was achieved with 0.12 wt.% catalyst. At 50 °C, the DS was lower but much less affected by the catalyst/starch ratio, thus the DS decreased from 0.15 to 0.08 as the amount of catalyst decreased from 0.5 to 0.05%. This is because at 90 °C Pd/TPPTS complex is unstable and decomposes progressively into palladium metal whereas at 50 °C the catalyst is stable enough. No palladium was detected in the modified polymer when the reaction was conducted in the presence of 0.05% palladium. An optimum DS of 0.06 suitable for application in latex preparation for decorative paints was obtained with 0.03% palladium at 50 °C.

The etherified starch was further transformed by hydrogenation of the double bonds to yield the corresponding linear octyl groups using $[RhCl(TPPTS)_3]$ a catalyst that is 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. Other catalytic transformations such as double bonds oxidation and olefin metathesis could possibly be used to prepare other modified starches for various applications.

6.6. Catalytic conversions to furan derivatives

The catalytic processes to obtain furan derivatives from carbohydrates and the catalytic routes from furan intermediates to chemicals and polymers have been reviewed by Moreau et al.



Scheme 20. Grafting of octadienyl chains on sucrose through butadiene telomerization.

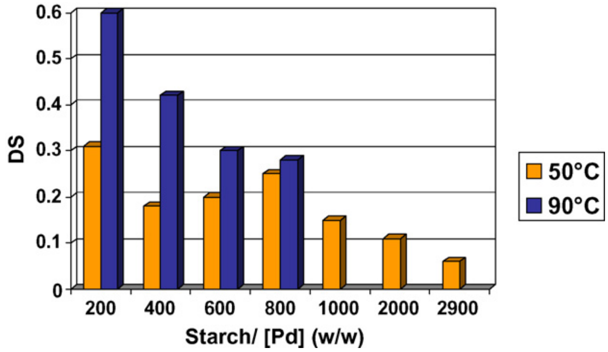


Fig. 5. Modification of starch by butadiene telomerization. Influence of the catalyst mass on the degree of substitution (DS).

[99]. From fructose **1** or carbohydrates based on fructose (sucrose, inulin), the first transformation step is a dehydration to 5-hydroxymethylfurfural **2**. Fructose dehydration in the presence of liquid and solid acids has been extensively studied with various solvents. DMSO is best suited because it prevents the formation of levulinic and humic acids [100,101]. Fructose dehydration at 165 °C was performed in the presence of dealuminated mordenite (Si/Al = 11) with a selectivity of 92% at 76% fructose conversion [102]. Starting from raw inulin hydrolysates for a better process economy, the selectivity to **2** was up to 97% at 54% conversion [103]. The fructose route to **2** has not been industrially developed, but **2** is actually synthesized by hydroxymethylation with formaldehyde of furfural **8** which is obtained industrially (200,000 t year^{-1}) by dehydration of pentoses and hemicelluloses (Fig. 6).

The hydrogenation of **2** in the presence of metal catalysts (Raney nickel, supported platinum metals, copper chromite) leads to quantitative amounts of 2,5-bishydroxymethylfuran **6** used in the manufacture of polyurethanes, or 2,5-bishydroxymethyltetrahydrofuran **7** which can be used in the preparation of polyesters [104]. However, investigations were more focussed on furfural **8** hydrogenation to furfurylic alcohol **9** avoiding the hydrogenation of the furan ring. Vapour phase hydrogenation of **8** can be advantageously carried out on copper catalysts supported on activated carbon [105] rather than with conventional copper chromite catalysts. Liquid phase hydrogenation at 80 °C in ethanol on Raney nickel modified by heteropolyacid salts resulted in a 98% yield to furfuryl alcohol [106].

Oxidation of 5-hydroxymethylfurfural **2** is used to prepare 2,5-furandicarboxyaldehyde **3**, used as a precursor of diamines and Schiff's bases, 5-formyl-2-furancarboxylic acid **4**, and 2,5-furandicarboxylic acid a potential substitute of terephtalic acid. Oxidation by air on platinum catalysts leads selectively to **4** but the oxidation proceeds further towards **5**, which is obtained quantitatively. [107]. The oxidation of **2** to dialdehyde **4** was achieved at 90 °C with air as oxidizing in the presence of V_2O_5/TiO_2 catalysts with a selectivity up to 95% at 90% conversion [108,109].

Numerous other furan monomers potentially used in the manufacture of polymers were described [99].

7. Catalytic conversion of lignocellulosic materials

Vegetables oils and most of the carbohydrates used to produce chemicals are issued from grains harvested primarily for food and feed and their productivity is rather low, e.g., 3–8 t of dry matter per hectare of cultivated land. In contrast,

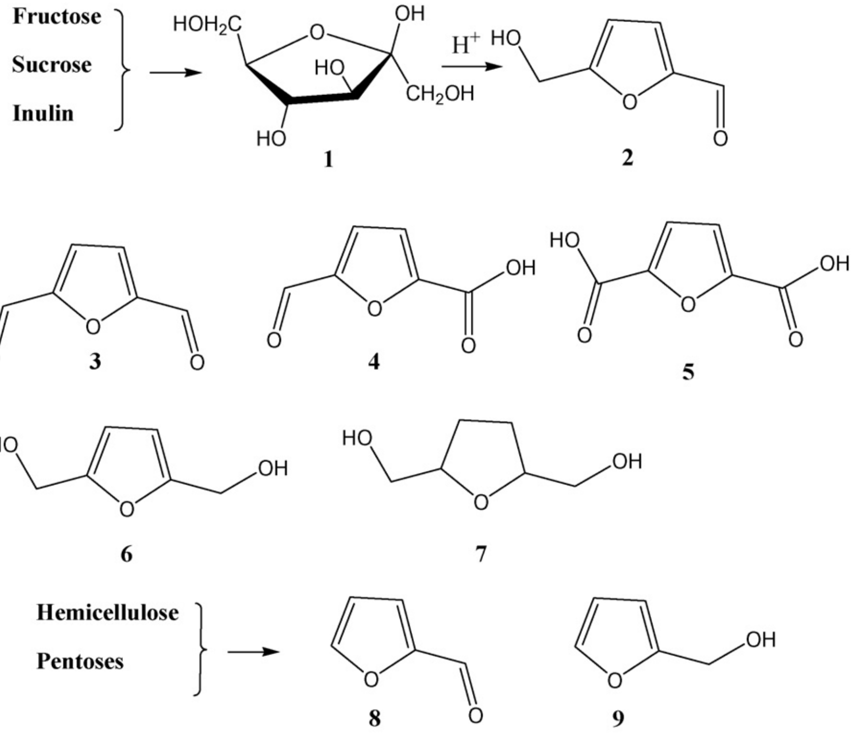


Fig. 6. Synthesis of furane derivatives from carbohydrates.

the non-grain portion of biomass, i.e., agricultural wastes (cobs, stalk, stovers) and vegetative biomass (trees, leaves, etc.) are hardly used so far to produce chemicals in spite of their much larger availability. Lignocellulosic materials are built on the intimate mixture of cellulose, hemicellulose and lignin that are difficult to separate and to process. Cellulose polymers are glucoside units connected via β-1,4-glycosidic linkages instead of α-linkages in the case of starch; they are more stable and difficult to hydrolyse by chemical or enzymatic way. Hemicelluloses are more easily hydrolyzed than celluloses and yield valuable pentoses such as xylose and arabinose. They are potentially a very important, largely untapped renewable source of chemicals. Lignins have a very complex polymeric structure based on interconnected aromatic derivatives and are very recalcitrant materials to process. Still chemicals such as vanillin can be obtained by catalytic oxidation of lignosulfonate [110]. So far catalysis plays a minor role to derive chemicals from lignocellulosic materials. Development must await progresses in cheaper depolymerization processes of cellulose and lignin based on improved biotechnologies.

8. Concluding remarks

Only few examples were selected in this paper from a very active field of basic research covering multidisciplinary topics published in a great diversity of journals. The R&D on biomass-derived products is also rapidly expending. Chemical companies have started extensive R&D efforts on developing biobased chemicals. According to the report ‘‘Vision for Energy and Biobased Products in the United States’’ [1] the share of target chemicals that are biobased could reach 25% by 2030. To meet the challenge a large integrated research effort in chemistry, biochemistry, and genetics as well as in chemical and biochemical engineering will be required.

In view of the diversity and complexity of the raw materials employed as feedstocks in bioproduct synthesis, the processes leading to end-products are necessarily different from present processes starting from fossil fuels. Although the cost of many platform molecules issued from biomass are comparable to those of many current chemical intermediates their processing costs is much higher. New flow sheets have to be developed to decrease the cost and to increase the quality of end-products, because even if they may prefer bio-based products, consumers do not want to pay more and have lower quality products. Flow sheets of organic synthesis from hydrocarbons have been improved for more than a century; it may require some time to reduce the processing costs of biomass derivatives to make competitive bio-products.

Catalysis has a major role to play at converting biomass into useful products. Presently, a comparatively limited number of researchers in Academia are active in this field. In view of the importance of environmental and economic challenges to meet, the workforce should be strengthened to develop this exciting field of research. Importantly, life cycle analysis studies should be conducted in parallel to validate the benefits of new processes in terms of ecology and economy.

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