

# Catalytic Technologies for the Conversion of Renewables

by Pierre Gallezot

The use of renewable raw materials for energy production and manufacture of chemicals is expected to gain importance in the future particularly in the countries of Latin America where land, sun and water are available. The advantages of using biomass instead of fossil fuels are briefly reviewed. Stress is laid on the production of speciality and fine chemicals via selective catalytic processes from triglycerides and carbohydrates containing crops. Examples of highly selective catalytic hydrogenation and oxidation processes starting from starch-derived feedstocks are given to illustrate the sustainable and green character of the chemistry based on renewables.

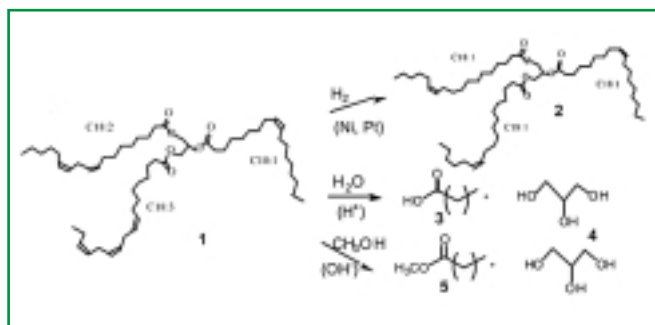


Figure 1 - Catalytic transformation of triglycerides

The use of non-fossil based renewable feedstocks to generate energy or to manufacture chemicals will become increasingly important in the 21<sup>st</sup> century. Using sun radiation energy photosynthesis process in plants produces huge amounts of renewable biomass, which can be used as alternative energy source avoiding the increase of atmospheric CO<sub>2</sub>. In contrast with fossil hydrocarbons, molecules issued from biomass are already highly functionalised so that less synthesis steps are required to produce final chemicals. They are also attractive because of the "natural" label and of their biodegradability. Extended use of renewable resources for the production of energy and chemicals would be particularly advisable in African, Asian and Latin America countries, where solar light and water supply are abundant enough to allow a fast growth of forest and crops.

After a short survey of the availability of renewables and of their catalytic conversion to bioenergy, this paper will deal with the main catalytic processes leading from crop-derived raw materials such as triglycerides and carbohydrates, to valuable intermediates or fine chemicals. This will be illustrated by studies of catalytic carbohydrate transformations carried out in our laboratory during the last few years.

## Renewables availability and catalytic conversion

The potential of biomass (crop, wood, animal waste and municipal waste) for energy production has been reviewed by

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Fischer and Schrattenholzer [1]. The bioenergy potential of the base year 1990 was estimated at 225 exaJ (10<sup>18</sup> Joules) or 5.4x10<sup>9</sup> toe and by year 2050 this potential is expected to grow between 370 and 450 exaJ. The global energy value from photosynthesis is estimated at 4,000 exaJ [2]. However, the theoretical potential is far from being realised, e.g., the actual use of bioenergy in 1990 was 46 exaJ. Higher yields of biomass in terms of dry matter per hectare can be obtained by replacing conventional crops for food production (cereals, triglyceride-containing crops, sugar) by new crops giving a higher yield of dry matter per area of cultivated land. Thus, according to Diamantis and Koukios [3] new crops based on sorghum or miscanthus give 3 to 4 time higher yields of dry matter per hectare than conventional crops used mainly for food production. In the same way, agro-forestry replacing conventional forest exploitation could provide a much higher yield of bioenergy per hectare of land.

Biomass is presently used for the production of energy either directly by combustion or indirectly by first converting it to bio-fuels via catalytic processes. Thus, enzymatic fermentation of sugar or cereals yields ethanol, which can be further converted by catalytic reforming to hydrogen. Transesterification of triglycerides by methanol in the presence of basic catalysts is used to produce the so-called biodiesel. The catalytic gasification of biomass by thermal treatment in the presence of various oxide catalysts leads to syngas and hydrogen. These catalytic processes, which are presently active subjects of research, are out of the scope of the present paper.

Instead of degrading the molecules issued from crops into C<sub>1</sub> molecules and hydrogen, it is wiser to use them as starting feedstock for the synthesis of high value added end-products,

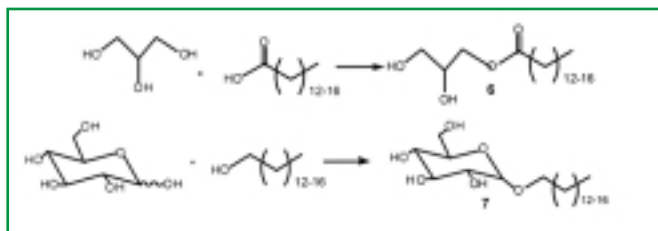


Figure 2 - Acid-catalysed synthesis of surfactants from triglyceride and carbohydrate derivatives

which requires much fewer synthesis steps than starting from fossil hydrocarbons.

The following sections will give a few examples of catalytic conversion of triglycerides and carbohydrates to produce various intermediates and speciality products.

## Main catalytic processes for the conversion of triglycerides

Triglycerides contained in soybean oil, palm oil, rapeseed, sunflower etc., are triesters of glycerol and unsaturated fatty acids. A model triester molecule 1 built from C<sub>18</sub> fatty acids with various degrees of unsaturation is given in Figure 1. The world production of triglycerides is ca. 105 Mt in year 2000, and increases by 5% each year.

About 85% of triglycerides are employed in the food industry as edible oils and fats. The triglycerides are partially hydrogenated to meet nutritional, stability and melting point specifications. Typically the fatty acids should not be hydrogenated to saturation, but should contain residual C=C bonds. The industrial hydrogenation process is essentially unchanged from the beginning of the 20<sup>th</sup> century. Nickel catalysts are still used in spite of the fact that *cis-trans* isomerisation of C=C bonds occurs during high temperature hydrogenation on nickel catalysts. *Trans* isomers have been pointed out to be unhealthy. It would be desirable to use more active platinum catalysts that give very little *trans* isomerisation particularly at low temperatures [4].

Triglycerides are converted to methyl ester 5 (Figure 1) by transesterification with short chain alcohols, particularly methanol. The fatty methyl esters are employed in increasingly higher amounts as additive to diesel acting both as fuel substitute and lubricant. The catalysts are soluble bases (typically NaOH or KOH), which tend to be replaced by basic inorganic solids, or organic bases immobilised on solids to allow an easier separation between catalyst and products.

Fatty monoesters of well defined composition are also prepared by esterification of alcohols with fatty acids 3 (Figure 1) produced by hydrolysis of triglycerides. They are used as biodegradable lubricants. Esterification with polyols such as glycerol or sucrose are used to prepare surfactants 6 (Figure 2). Fatty esters are also used to obtain fatty alcohols by hydrogenation in the presence of metallic catalysts. Copper chromite catalysts used in the past are now replaced by ruthenium catalysts giving improved activity, selectivity, and stability to leaching. Selective hydrogenation of the ester without hydrogenation of the C=C bond is particularly difficult. Thus, methyl oleate was hydrogenated to oleyl alcohol with 50% selectivity on Ru-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts [5].

Fatty alcohols are widely used to prepare biodegradable surfactants, e.g., alkyl glucoside 7 (Figure 2) obtained by acetali-

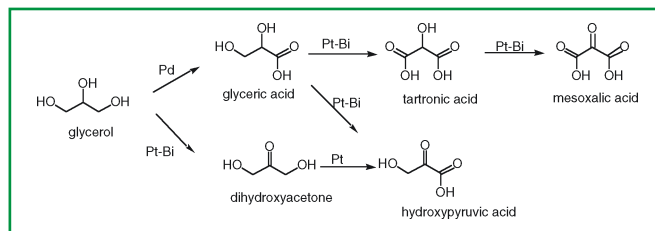


Figure 3 - Products obtained by catalytic oxidation with air of glycerol aqueous solutions [10]

sation with glucose or sucrose on acid catalysts. The present trend is to replace soluble acidic catalysts by acidic solids which can be separated from the medium.

Taking advantage of the presence of C=C bonds along the fatty chains a great varieties of valuable chemicals and polymers can be obtained via catalytic dimerisation or epoxidation reactions. A short review of oleochemicals derived from triglycerides can be found in [6].

Glycerol is produced in large amounts as by-product of triglyceride transesterification and hydrolysis reactions (Figure 1). It can be valorised in the synthesis of various chemicals:

- surfactants or emulsifier, prepared by esterification with fatty acid or transesterification with triglycerides;
- 1,3 propanediol by enzymatic or catalytic conversion;
- oxidation products which can be used as synthons or end-products for various applications.

Thus, the catalytic oxidation with air of glycerol in the presence of Pt- or Pd-catalysts promoted with bismuth leads to various chemicals described in Figure 3 [7-10].

## Selected examples of catalytic carbohydrate conversion

A sustainable economy requires the development of processes for the production of chemicals from renewable resources. This approach is particularly rational for the synthesis of intermediates and fine chemicals from molecules extracted from polysaccharide-containing crops. Figure 4 gives a summary of the various catalytic reactions on starch-derived carbohydrates carried out at Institut de Recherches sur la Catalyse during the last ten years. Starch 1 is a natural polymer extracted from maize, wheat, potato, and manioc crops. Hydrolysis by chemical or enzymatic routes yields glucose 2, which has been used as starting material for the synthesis of various molecules.

Hydrogenation of glucose leads to sorbitol 3 used as additive in food industry and in a varieties of manufactured products, and as building block in organic synthesis, e.g., for vitamin C. About 700,000 t/y of sorbitol are produced mainly by hydrogenation in batch reactor in the presence of Raney nickel catalysts. The activity and stability of these catalysts have been improved by using multimetallic formulations [11], however, it is desirable to design continuous hydrogenation processes based on ruthenium catalysts which are more active and less prone to leaching in reaction medium than nickel. Studies have been conducted at IRC to design a continuous process in trickle-bed reactor using a fixed bed of Ru/C catalysts supported on Norit extrudates [12]. The hydrogenation of 40 wt% water solution of glucose at 100 °C under 80 bar H<sub>2</sub>-pressure on 1.8% Ru/C catalyst yielded more than 99% sorbitol with a stable activity for 690 hour on stream. However, the domain of contact time where the 99% yield was obtained was very

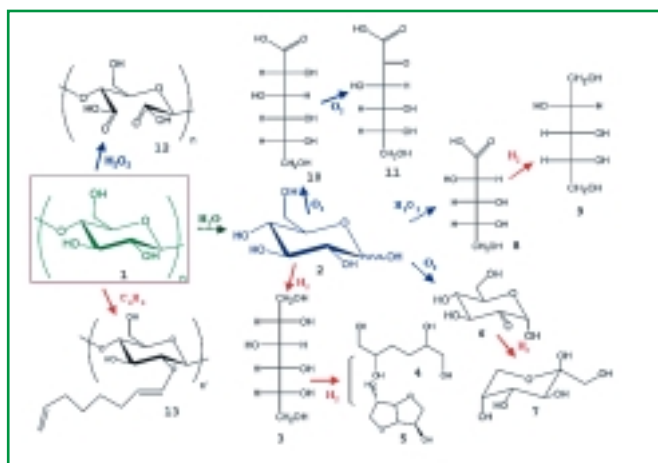


Figure 4 - Catalytic reactions from starch investigated at IRC

narrow because of sorbitol epimerisation into mannitol. The process was improved by designing bimetallic Ru-Pt/C catalysts with very homogeneous particle size and composition, which gave 99.5% sorbitol yield within a large domain of contact time, and a productivity of 2 t/day/kg(catal) [13]. There is a great interest to convert C<sub>6</sub> carbohydrates into C<sub>5</sub> polyols used as food or care products additives. Thus, glucose available in large supply from renewable resources can be converted via a two step process to arabitol 9 (Figure 4). The first step is an oxidative decarboxylation of glucose into arabinonic acid 8 in the presence of soluble basic catalysts. Arabinonic acid in aqueous solutions is in equilibrium with the corresponding  $\gamma$ -lactone and  $\delta$ -lactone. The second step is the catalytic hydrogenation of arabinonic acid and lactones to obtain arabitol. We have recently achieved the first in depth study on the kinetic of this reaction and on the factors affecting its selectivity [14, 15]. Table 1 gives the product distribution obtained in the hydrogenation of 20 wt% aqueous solu-

tion at 100 °C on Ru/C catalysts. Hydrogenation of pure solution gives 93.6% selectivity to arabitol with a high proportion of undesirable deoxy-products. It was shown that the addition of sodium anthraquinone-2-sulfonate (A2S) improved the selectivity from 93.6 to 96.7% because the promoter decreased the rate of unwanted dehydroxylation reactions. A2S acted as permanent surface modifier since the catalyst was recycled with the same selectivity without further addition of A2S. This study paved the way for further studies on reduction of carboxylic acids and lactones in carbohydrate chemistry.

Although many applications in food and fine chemical industries require products of high purity there are potential markets for mixture of carbohydrate derivatives. Thus, in the framework of the EC programme FAIR [16], starch was converted into mixtures of polyols [17] that could be used in the manufacture of polyesters, alkyd resins, and polyurethanes employed in paints, powder coatings, and construction materials. Deoxyhexitols consisting of C<sub>6</sub> diols, triols, and tetrols, obtained by partial dehydroxylation of hexitols are adapted for the targeted applications, but they are not available commercially at a reasonable price.

Since sorbitol can be easily obtained by hydrogenation of starch hydrolysates this molecule was chosen as starting material for hydrogenolysis studies. Copper-based catalysts, which have a low activity for hydrogenolysis of C-C bonds, were employed to catalyse the dehydroxylation reactions leading to deoxyhexitols. A 64.5% selectivity was obtained at 180 °C (Table 2) and measurement of the total organic carbon indicated that there was no loss of carbon-containing molecules. The mixture of polyols obtained was employed as such to prepare alkyd polymers, which were used in the manufacture of gloss paint. The final product showed satisfactory specifications except for a too low viscosity and too long drying time; these specifications could be improved by distillation of ethylene and propylene glycol from the mixture. The latter could be recovered and used in their current markets. Also,

Table 1 - Product distribution of arabinonic acid hydrogenation on Ru/C catalyst

Solution	Initial rates mmol h <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup>	Selectivities at 98% conversion					
		arabitol	deoxy	ribitol	xylitol	erythritol	threitol
1	460	93.6	4.2	0.6	0.4	1.1	0.1
2	133	97.9	0.6	0.5	0.2	0.7	0.1

1: 20 wt% aqueous solution of arabinonic acid,  $\gamma$ - and  $\delta$ -lactones ([acid]/[lactones] = 0.85); 2: solution 1 + 2,180 ppm of sodium anthraquinone-2-sulfonate

Table 2 - Product distribution obtained by hydrogenolysis of sorbitol solutions at 180 °C on CuO-ZnO catalysts

Analysed products	Selectivity % *
Ethylene glycol	6.7
1,2-propanediol	8.1
Glycerol	12.1
Deoxytetritols (1,2-butanediol; 1,3-butanediol; 1,4-butanediol; 2,3-butanediol; 1,2,3-butanetriol)	2.0
Tetritols (threitol, erythritol)	3.3
Deoxypentitols (2,4-pentanediol; 1,2-pentanediol; 1,4-pentanediol)	2.7
Pentitols (xylitol, arabitol, ribitol)	0.6
Deoxyhexitols (1,2-hexanediol; 1,6-hexanediol; 1,2,3-hexanetriol; 1,2,6-hexanetriol; 1,2,4,6-hexanetetrol)	64.5

\* at 90% conversion

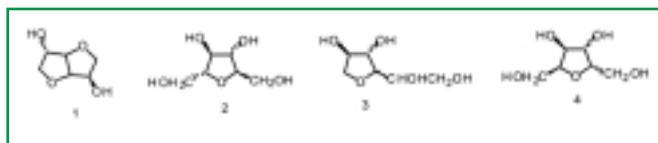


Figure 5 - Polyols obtained by catalytic dehydrocyclisation of aldols

sorbitol solutions were dehydrocyclised at 200 °C in the presence of Pd-catalysts to obtain cyclic polyols useful for the same application. A 90% yield of 1,4,3,6-dianhydrosorbitol 1, 2,5-anhydromannitol 2, 1,4-anhydrosorbitol 3, and 2,5-anhydroiditol 4 (Figure 5) was obtained [18].

Gluconic acid (10, Figure 4), used as a biodegradable chelating agent and as an intermediate in the food and pharmaceutical industry, is produced by enzymatic oxidation of glucose. Alternatively glucose oxidation can be conducted on heterogeneous metal catalysts using air as oxidising agent. Besson *et al.* [19] have studied the oxidation of 1.7 mol l<sup>-1</sup> glucose solution at pH 9, on carbon-supported palladium catalysts with different particle sizes.

The catalyst with particles larger than 3 nm gave a complete conversion within 6 h, whereas the conversion reached a plateau at two-thirds conversion on the catalyst with particles smaller than 2 nm. This was attributed to a particle size dependent, oxygen poisoning of the surface, the smaller particles being the most prone to over-oxidation because of their stronger affinity for oxygen.

The beneficial effect of bismuth on the activity and selectivity was clearly demonstrated with Pd-Bi/C catalysts of homogeneous size and composition (5 wt% Pd, Bi/Pd = 0.1) prepared by deposition of bismuth on the surface of 1-2 nm palladium particles via a redox surface reaction [20]. The rate of glucose

oxidation to gluconate was 20 times higher on Pd-Bi/C catalysts (Bi/Pd = 0.1) than on Pd/C. Table 3 gives the product distribution in four successive catalyst recycles. The selectivity remained very high on recycled catalysts and it was verified that bismuth did not leach in solution. These results were interpreted in terms of bismuth protecting palladium from over-oxidation because of its stronger affinity for oxygen, as evidenced by calorimetric measurements. It was proposed that bismuth acted as a co-catalyst according to the mechanism given in Figure 6.

Oxidation of gluconic acid with air carried out on bismuth-promoted catalyst yielded 60% of 2-ketogluconic acid (11, Figure 4) when the reaction was conducted at pH 7 [21], but at acidic pH, the yield was 98% [22]. Bismuth atoms on the surface of platinum favour oxidation selectivity in  $\alpha$ -position of the carboxylic acid function as described in Figure 6. In the absence of bismuth, glucaric acid (oxidation on C<sub>6</sub> carbon) was the main oxidation product.

In all preceding examples catalytic reactions were performed in triphasic medium with the organic substrates (products and educts) dissolved in the liquid phase and heterogeneous catalysts in suspension or fixed-bed.

In contrast, in a recent project [23], it was attempted to perform chemical modifications of insoluble native starch via catalytic route to modify its hydrophilic properties in order to meet specifications for its use as additive in paper or paint industries. Selective oxidation of vicinal diols on C<sub>2</sub> and C<sub>3</sub> of the glucose unit leading to dicarboxylic acids (12, Figure 4) was achieved with H<sub>2</sub>O<sub>2</sub> in the presence of soluble iron phthalocyanine catalysts [24].

In contrast, to make starch less hydrophilic for application in paint industry, OH groups were etherified by butadiene telomerisation in the presence of soluble palladium catalysts, which

Table 3 - Product distribution of glucose oxidation with air on bismuth-promoted palladium catalysts

Catalyst <sup>a</sup> (run)	Conversion <sup>b</sup> (%)	Yield /mol%				Selectivity (%)
		1	2	3	4	
PdBi/C (1 <sup>st</sup> )	99.6	99.4	<0.4	<0.4	0.2	99.8
PdBi/C (2 <sup>nd</sup> )	99.7	98.9	<0.4	0.6	0.2	99.1
PdBi/C (3 <sup>rd</sup> )	99.8	98.5	0.4	0.8	0.2	98.7
PdBi/C (4 <sup>th</sup> )	99.9	98.5	0.4	0.7	0.2	98.6
PdBi/C (5 <sup>th</sup> )	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

a: 4.7 wt% Pd; Bi/Pd=0.1. b: after 155 min on PdBi/C and 24h for Pd/C; 1: D-gluconate; 2: 2-keto-D-gluconate; 3: 5-keto-D-gluconate + D-glucarate, 4: D-fructose; reaction conditions: 1.7 mol l<sup>-1</sup>, T = 313K, pH 9; [glucose]/[Pd] = 787; air at atmospheric pressure.

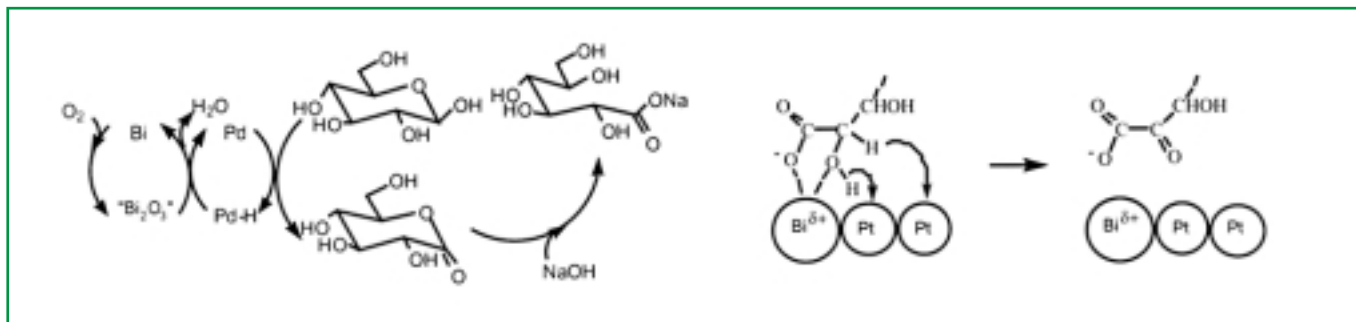


Figure 6 - Left field: proposed mechanism of glucose oxidation on Pd-Bi catalysts [20]. Right field: proposed mechanism for the Bi-promotion of oxidation in  $\alpha$ -position of carboxylic acid



results in lateral unsaturated hydrocarbon chains grafted on starch macromolecular chains (13, Figure 4). This catalytic reaction was described in detail in the case of sucrose etherification [25].

## Conclusions

The main advantages, beside their renewability, of employing raw materials issued from crops and biomass for manufacturing chemicals are the high molecular functionality, the biodegradability and the natural label which are retained from the initial feedstock to the end-products. For specific crops providing well defined molecules (terpenes, triglycerides, carbohydrates) the priority should be given to their transformation into high value added intermediate and fine chemicals while other biomass composants (wood and crop residues, animal and municipal waste) should rather be degraded into smaller molecules by fermentation or gasification for energy production.

The catalytic conversions of carbohydrates discussed in this article provide a good example of sustainable and green chemistry.

The hydrogenating and oxidising agents ( $H_2$ ,  $O_2$ ,  $H_2O_2$ ), the solvent ( $H_2O$ ), the mild temperature conditions, and the biodegradability of organic substrates (product and educts) allow the development of environmentally friendly processes. Heterogeneous catalysts allow a great productivity and easy process development (one pot reaction, continuous operation).

Their selectivities may in some cases, such as glucose oxidation, equal or surpass those of enzymatic reactions. The combined use of catalytic processes (heterogeneous, homogeneous, enzymatic) is advisable to achieve multistep transformations. Homogeneous processes are necessary to transform natural polymers such as starch or cellulose.

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