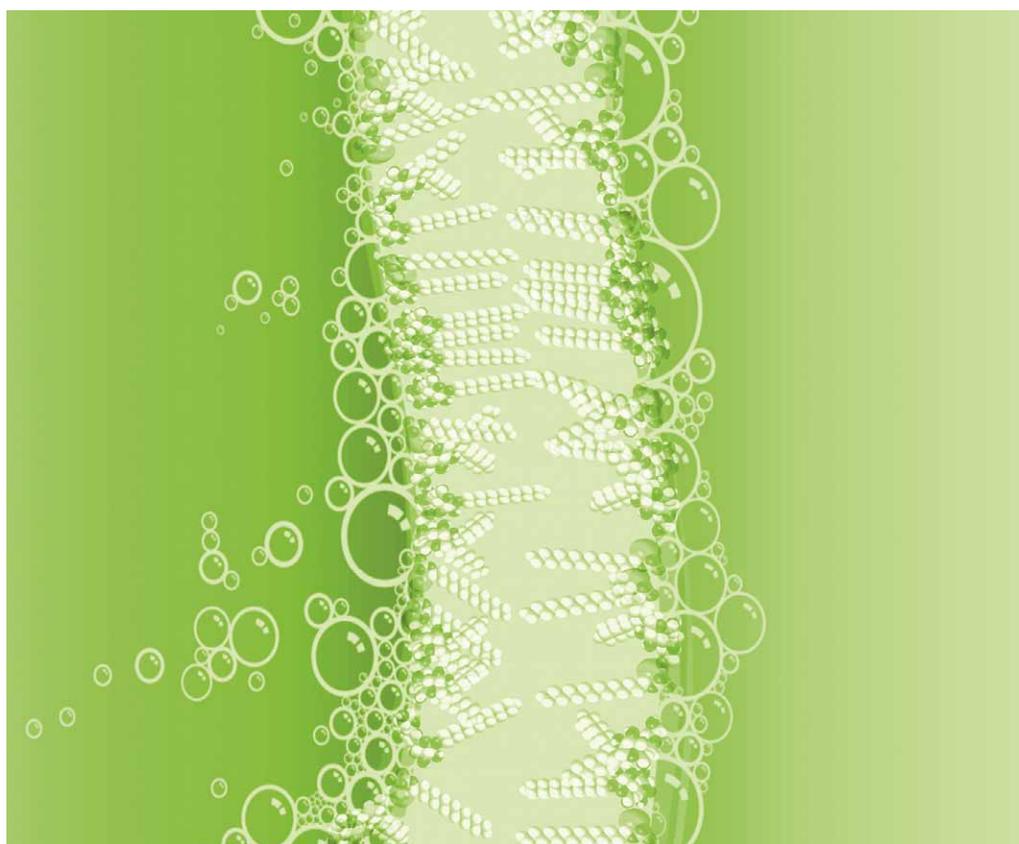


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## CRITICAL REVIEW

## Conversion of biomass to selected chemical products†

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This *critical review* provides a survey illustrated by recent references of different strategies to achieve a sustainable conversion of biomass to bioproducts. Because of the huge number of chemical products that can be potentially manufactured, a selection of starting materials and targeted chemicals has been done. Also, thermochemical conversion processes such as biomass pyrolysis or gasification as well as the synthesis of biofuels were not considered. The synthesis of chemicals by conversion of platform molecules obtained by depolymerisation and fermentation of biopolymers is presently the most widely envisioned approach. Successful catalytic conversion of these building blocks into intermediates, specialties and fine chemicals will be examined. However, the platform molecule value chain is in competition with well-optimised, cost-effective synthesis routes from fossil resources to produce chemicals that have already a market. The literature covering alternative value chains whereby biopolymers are converted in one or few steps to functional materials will be analysed. This approach which does not require the use of isolated, pure chemicals is well adapted to produce high tonnage products, such as paper additives, paints, resins, foams, surfactants, lubricants, and plasticisers. Another objective of the review was to examine critically the green character of conversion processes because using renewables as raw materials does not exempt from abiding by green chemistry principles (368 references).

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† Part of a themed issue covering the latest developments in green chemistry.



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## 1. Introduction

Apart from providing food, feed and energy, biomass was employed throughout recorded history to extract valuable products such as medicinal drugs and flavours and fragrances. However, it was only during the second half of the 19th century that large scale industrial conversion of biomass to chemicals and materials started with the production of cellulose esters (nitrate and acetate) and oxidised linseed oil (linoleum). During the last century flavours and fragrances were produced by catalytic conversion of terpenes, lubricants and surfactants were produced by the oleochemical industry from vegetable oils, and a large number of industrial products were obtained by conversion of carbohydrates obtained from various crops. However, bio-based chemicals suffered a severe economic competition from much cheaper products synthesised by conventional routes from hydrocarbons that were optimised steadily for more than 100 years.

The interest in biomass conversion to chemicals increased sharply during the last ten years within industrial companies and Academia with the support of international and national agencies. Chemical manufacturers worldwide became interested in renewable feedstocks for producing bulk and specialty chemicals, while start-up and SME companies developed innovative processes to produce chemicals and materials in niche markets. The Academic community subsidised by national and multinational programmes followed the momentum to such an extent that the number of journal articles dedicated to biomass conversion to chemicals increased dramatically during the last

four years; thus, it doubled from 2007 to 2009 and from 2008 to 2010 (source: Web of Science). Extensive literature surveys covering this subject were published in journals<sup>1–8</sup> and books<sup>9–11</sup> a few years ago, and a review focussing on the conversion of carbohydrates over heterogeneous catalysts was published recently.<sup>12</sup>

Interest in the biomass-to-chemical value chain raised as the chemical industry accelerated the development of sustainable manufacturing processes,<sup>13–18</sup> but R&D was also propelled by two global issues, *viz.*:

1. The necessity to use renewable carbon sources aimed at compensating the expected decrease of petroleum production. Concern about the chaotic oil market price was also put forward to advocate the need for alternative carbon resources. These are strong arguments as far as transportation fuels are concerned, but they are less convincing for the manufacture of chemicals because only *ca.* 5% of the total oil production are currently sufficient to provide the carbon needed to synthesise organic chemicals and polymers.<sup>19,20</sup>

2. The need to decrease greenhouse gas (GHG) emissions suspected to have a detrimental effect on the global climate by employing renewable carbon available from biomass. This is also a frail argument in the case of chemicals comparatively to the huge GHG emissions associated with energy and fuel consumption. Furthermore, GHG emissions depend critically upon many parameters including agricultural practices, biomass collection, and conversion process so that the extent of GHG reduction is debated.<sup>21</sup>

Clearly, the current move of the chemical industry to substitute a growing part of fossil feedstocks by renewable carbon is not pushed only by the fear of dwindling fossil resources or global warming, there are other driving forces at stake, *viz.*:

1. A sustainable production of chemicals from biomass should contribute to improve the public confidence in the chemical industry.

2. Industrially driven agencies in developed countries such as SusChem<sup>22</sup> in Europe or US government agencies<sup>23</sup> have actively promoted the use of renewable resources to manufacture innovative products that could preserve the competitiveness of the chemical industry in a global market economy.

3. Bio-based bulk chemicals have a market potential<sup>7,24</sup> and bio-based products such as surfactants, lubricants, plasticisers have already a sizable market share.<sup>25</sup>

4. In addition to merely duplicating existing products derived from fossil resources, the chemistry from renewables opens an opportunity to develop a new portfolio of products that have no equivalence among those presently manufactured by classical synthesis routes from hydrocarbons.

5. A subsidiary advantage is that the development of bio-products requires less legislative constraints. Thus, biopolymers, even chemically modified, are presently exempted from the European REACH registration.<sup>26</sup>

The present review deals with the production of chemicals and materials from biomass excluding conversion processes to fuels. Thermochemical processes such as gasification, pyrolysis and aqueous phase reforming of biomass are out of the scope of this review although they could provide some opportunities for the production of chemicals. Thus, biomass gasification

yields syngas, which, depending on the nature of heterogeneous catalysts, can be selectively converted to hydrocarbons, dimethylether, methanol, and even higher alcohols.<sup>1,27,28</sup> Fast pyrolysis leads to a complex mixture of oxygenates that could be employed to extract chemicals although the recovery of pure compounds would be very costly.<sup>29</sup> The hydroprocessing of pyrolysis oils on Ru/C and Pt/C catalysts increased the amounts of polyols and alcohols.<sup>30</sup> Aqueous phase reforming of carbohydrates was mainly dedicated to alkane and hydrogen production,<sup>31</sup> but it was shown that dehydration and coupling reactions lead to the transient formation of oxygenates which could be valuable chemicals.<sup>32–34</sup>

The catalytic transesterification of triglycerides leading to biodiesel or the various combined depolymerisation/fermentation processes leading to bioethanol or biobutanol will not be treated. Bio-catalytic processes are of primary importance for the production of platform molecules from carbohydrates.<sup>35,36</sup> In many instances biomass conversion requires a combination of bio- and chemo-catalytic processes either carried out separately, or in one-pot processes as illustrated by the concept of cascade catalysis.<sup>37–39</sup> However, in view of the abundant literature on bio-conversion processes this important topic is out of the scope of the present review.

According to a classification proposed in two previous papers,<sup>40,41</sup> three conversion strategies described in Fig. 1 will be examined and illustrated by recent investigations, *viz.*:

1. Biomass is converted by depolymerisation and/or fermentation into platform molecules that are subsequently employed as building blocks for the synthesis of intermediates and fine chemicals *via* heterogeneous and/or homogenous catalytic processes.

2. Biomass is converted in one or few steps to a mixture of molecules with similar functionalities that are used without separation for the manufacture of high tonnage end-products.

3. Biopolymers are chemically modified in one step to introduce new functionalities along the polymer backbone.

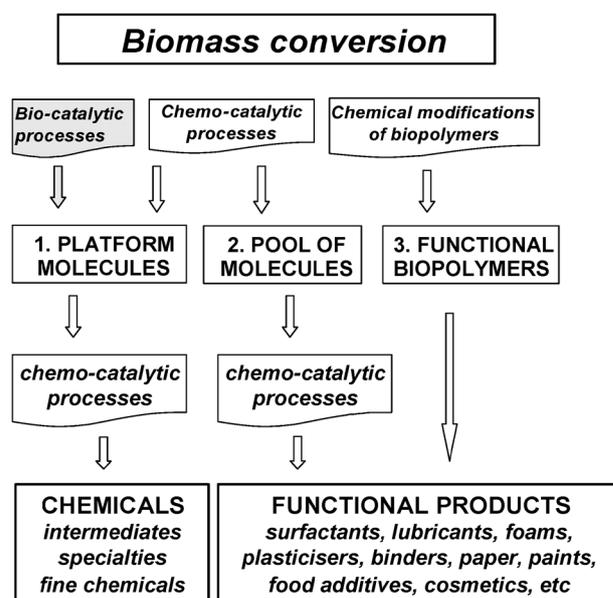


Fig. 1 Strategies of biomass conversion processes. Bio-catalytic processes were out of the scope of the present review.

The functional biopolymers can be incorporated in high tonnage end-products.

A major objective of this review which is part of a general issue on green chemistry is to address critically the environmental sustainability of biomass-to-chemical value chains. The use of renewable feedstock is #7 in the list of green chemistry principles, but biomass conversion processes should not ignore the 11 other principles.<sup>42,43</sup> Life cycle analysis (LCA) is the required tool to evaluate the environmental impact of biomass conversion to chemicals, however because of the multiplicity of feedstocks, processes and targeted chemicals, there are few LCA dedicated to that subject.<sup>44–49</sup>

Another objective of the review was to examine economic issues, which together with environmental assessment are essential for the sustainability of the biomass-to-bioproducts value chain. Indeed biomass conversion processes should not ignore basic economy principles including feedstock availability and price, competition with food needs, energy requirements, waste management, and hazards.<sup>18</sup> Interestingly, large industrial companies were well ahead of the Academic community for monitoring the environmental, economic and societal sustainability of chemical production from biomass. Thus, the BASF company developed very early various assessment tools such as “Eco-efficiency Analysis” or “Seebalance” probing the sustainability of biomass conversion processes to chemicals in comparison with conventional processes.<sup>44,48</sup>

## 2. Strategies of biomass conversion

The biorefinery concept dating back from the turn of the century<sup>50</sup> was the subject of various definitions during the last decade.<sup>51</sup> As per the International Energy Agency, Bioenergy-Task 42, biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy, however a biorefinery could even be restricted to a single process, typically sugar fermentation to ethanol.<sup>52</sup> There is abundant literature on biorefineries dedicated to biofuel production, but biorefineries focussing on bioproducts were also documented.<sup>16,53–57</sup> Actually, biorefineries dedicated to the processing of starch, sucrose or vegetable oils to bioproducts have been in operation well before the biorefinery concept was coined. Large starch biorefineries established decades ago have been processing million tons per year of corn, wheat or potato starch to produce hundreds of different products. Thus, Roquette company is currently treating 6 Mega tonnes per year of starch-containing crops to produce over 700 different products.<sup>58</sup> Cognis company established 150 years ago in Germany is producing hundreds of different wellness, nutritional and functional products from vegetable oils.<sup>59</sup> Presently, a multitude of start-up and SME companies are burgeoning to exploit new resources such as microalgae or sea weeds and to develop optimized fermentation processes to produce platform molecules that will be used as building blocks for chemistry.<sup>60</sup> New biorefineries are currently established to process lignocellulosic materials from forestry products, various types of grasses (miscanthus, switchgrass) and agricultural residues.<sup>16,61–67</sup> An interesting trend coming from Nordic countries is the transformation of paper pulp mills into lignocellulose biorefineries achieving the collection of raw materials and the extraction of various wood

components such as lignin, cellulose, hemicellulose, tall oil and turpentine.<sup>6,68</sup>

Cost effective processes adapted to the molecular structure of highly functionalised biomass molecules have to be developed to make the quality and price of chemicals competitive with respect to products obtained by traditional routes from fossil fuels.<sup>18,24,35,53</sup> Robust and easily regenerated catalysts should be developed because natural raw materials may contain impurities, which could alter their selectivity and decrease their activity thus hampering catalyst recycling or continuous processes.<sup>41</sup> Rinaldi and Schüth<sup>69</sup> have outlined the various challenges facing the design of heterogeneous catalysts in biomass processing. A major issue is to develop multifunctional catalysts such as multi-site solid catalysts which could be used in cascade-type reactions allowing process intensification.<sup>70</sup> The combination of homogeneous and heterogeneous catalytic processes allowing a multi-step conversion of biomass as shown in the conversion of sucrose to various C<sub>5</sub>-oxygenates is desirable.<sup>71</sup> Cascade catalysis involving enzymatic and chemo-catalytic steps is an additional challenge.<sup>37–39</sup> New reaction media such as ionic liquids,<sup>63,72–74</sup> molten salt hydrates,<sup>75</sup> supercritical fluids<sup>76–78</sup> and microwave activation<sup>79</sup> should be employed to improve reaction processes. According to Bozell and Petersen<sup>55,56</sup> two different strategies can be selected to achieve biomass conversion to chemicals, *viz.*:

1. A target-driven approach employing process analysis methodology designed to find the most efficient synthetic routes to produce a given chemical starting from well-identified platform molecules. This approach may result in an uneconomical production of chemicals with respect to well-optimised, conventional synthesis routes from hydrocarbons.

2. A process-driven approach whereby biomass is converted by one or more catalytic processes (hydrogenation, hydrolysis, oxidation, *etc.*) yielding a family of valuable products. This approach is not intended to duplicate chemicals currently produced from fossil resources and could be more effective to find rapidly new valuable bioproducts.

Section 3 will provide examples of the catalytic conversion of platform molecules to pure isolated chemicals, while Sections 4 and 5 will illustrate the process-driven approach leading to a mixture of molecules or modified biopolymers that can be used without further separation for the manufacture of high tonnage end-products such as paper, paints, resins, foams, lubricants, plasticizers, cosmetics, *etc.* and functional materials for the manufacture of high tonnage functional end-products.

## 3. Conversion *via* platform molecules

In 2004 the US Department of Energy released a list of “Top 10 chemicals” (actually 15), which could be employed as platform molecules or building blocks for the synthesis of bio-based chemicals.<sup>80</sup> Among the “Top 10”, some were the subject of intense research and development during the past few years while there was a comparatively modest interest for organic acids such as fumaric, malic, aspartic, glutamic and itaconic acids. Based on this and other criteria, Bozell and Petersen<sup>56</sup> established a revisited list of top chemical opportunities including ethanol, furans, glycerol, lactic acid,

succinic acid, hydroxypropionic acid/aldehyde, levulinic acid, sorbitol and xylitol. Platform molecules are also available from terpenes and proteins. Thus,  $\alpha$ -pinene and  $\beta$ -pinene extracted from turpentine oil (350 000 tonnes per year), limonene extracted from citrus oil (30 000 tonnes per year) are platform molecules for the synthesis of flavours and fragrances and pharmaceuticals.<sup>81,82</sup> According to Sanders *et al.*<sup>53,83,84</sup> vegetal proteins or distiller grains available in large amounts as by-products of carbohydrate fermentations could become a large source of amino-acids that have a high potential as building blocks for fine and specialty chemicals.

The present review cannot provide a complete account on the abundant literature covering the conversion of all platform molecules. Thus the chemistry from glucose and sucrose platforms,<sup>2,12,85,86</sup> and from terpenes,<sup>2,81,82,87</sup> which were well documented in previous reviews will not be treated. Focus will be laid on platform molecules that were extensively studied in the past few years such as 5-hydroxymethylfurfural, furfural, levulinic, lactic and succinic acids, as well as new industrial derivatives from sorbitol. The glycerol platform was also the subject of many investigations but recent reviews cover these developments.<sup>88–92</sup> Still the craze for the glycerol platform deserves some comments. The sustainability of some investigations<sup>93,94</sup> aimed at producing syngas without questioning energy requirements and environmental issues in terms of CO<sub>2</sub> emission and waste generated is questionable. Glycerol is a wonderful platform molecule from which many useful intermediates or specialty chemicals can be produced but its availability could be overestimated. Glycerol finds hundreds of applications as food and feed ingredients, and in cosmetics, pharmaceuticals, explosives, *etc.*, and it is now used for the industrial production of intermediates such as epichlorohydrin<sup>95</sup> and propylene glycol.<sup>96</sup> Investigations on glycerol conversion were often justified by the necessity to use the increasing surplus of glycerol formed as a co-product of biodiesel production from plant oils. However, plant oils are primarily used to cover increasing food needs and the rest is also used for the expending oleochemical industry. As the glycerol demand is continuously increasing the market price of high grade glycerol suitable for chemical applications will stay at a level hardly compatible with an economic production of high tonnage intermediates. Unless abundant and cheap new sources of triglycerides become available, *e.g.* from algae, glycerol should rather be used as a platform to produce high value added chemicals.

### 3.1 5-Hydroxymethyl furfural (5-HMF) platform

**3.1.1 Synthesis of 5-HMF from carbohydrates.** 5-HMF and its derivatives levulinic acid, 2,5-bis(hydroxymethyl)-furan (2,5-BHF), 2,5-diformylfuran (2,5-DFF) and 2,5-furandicarboxylic acid (2,5-FDCA) were identified early as very promising chemical intermediates obtained by the catalytic conversion of carbohydrates based on C<sub>6</sub> units (Fig. 2).<sup>97</sup> 5-HMF was obtained by dehydration of fructose in the presence of soluble or solid acid catalysts or from glucose or even polysaccharides by more complex catalytic systems and reaction media.<sup>12,74,98–101</sup> The key issue was to prepare 5-HMF with economically acceptable processes that could be scaled up at the industrial level.

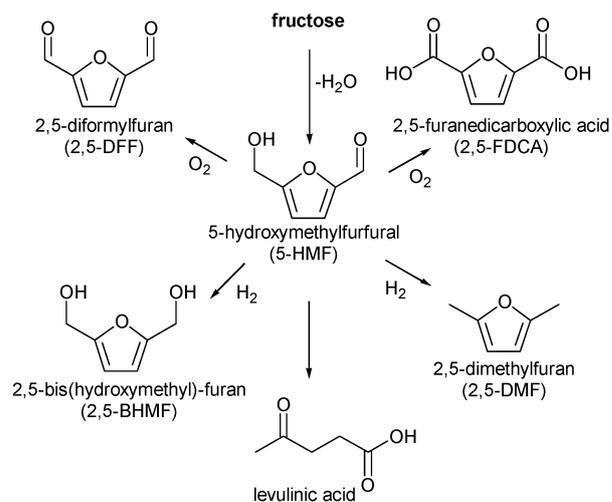


Fig. 2 Main 5-HMF derivatives.

This is not yet achieved in spite of intensive research efforts conducted in the past few years. The present review will compare the different catalytic systems and solvents employed for the 5-HMF production and examine their relevance to green chemistry.

It was shown earlier that the dehydration of aqueous solutions of fructose in the presence of liquid or solid acid catalysts resulted in modest yields to 5-HMF because of the formation of levulinic acid, formic acid and humins.<sup>102,103</sup> Dehydration at a short contact time of 27 wt% aqueous solution of fructose acidified with HCl by microwave heating yielded 63% of 5-HMF at 52% conversion.<sup>104</sup> The use of organic molecules such as methyl isobutyl ketone acting as an extracting solvent increased the 5-HMF yield. Thus, a 74% yield was obtained in batch mode in a mixture of water and methyl isobutyl ketone (MIBK) in the presence of dealuminated mordenites at 165 °C.<sup>105</sup> A continuous process based on the counter-current extraction of 5-HMF from the aqueous phase resulted in a 10% increase in selectivity because the residence time of 5-HMF in the aqueous phase was shortened.<sup>106</sup> It was shown earlier that high yield of 5-HMF can be obtained by conducting fructose dehydration in dimethyl sulfoxide (DMSO) to avoid the formation of side-products,<sup>107</sup> but there was a risk of formation of sulfur-containing, toxic compounds at the temperature required for DMSO distillation.<sup>100</sup> A selectivity of 72.8% at 93.6% conversion was attained in the presence of sulfated zirconia catalyst in a mixture of DMSO and acetone.<sup>108</sup> In supercritical water–acetone mixtures acidified with H<sub>2</sub>SO<sub>4</sub>, a 77% selectivity was obtained at 90% fructose conversion; it was mentioned that 5-HMF could be produced at 2 £ kg<sup>-1</sup> provided fructose is available at 0.5 £ kg<sup>-1</sup>.<sup>109</sup> Fructose dehydration catalysed by HCl in water/DMSO solutions in the presence of MIBK/*n*-butanol as an extracting organic phase yielded 5-HMF with an 89% selectivity at 95% conversion.<sup>110</sup> As HCl was replaced by a bifunctional mesoporous SBA-15 catalyst a lower yield of 5-HMF was obtained.<sup>111</sup> Binder and Raines<sup>112</sup> reported a 92% yield to 5-HMF as fructose was dehydrated with H<sub>2</sub>SO<sub>4</sub> catalyst in *N,N*-dimethylacetamide (DMA) solution with LiBr or KI additives. The same authors reported an 80% yield from

glucose with an even more complex system involving the mixture HCl–CrCl<sub>2</sub>–DMA–LiBr.<sup>112</sup>

The conversion of carbohydrates to 5-HMF in ionic-liquids was actively investigated and thoroughly reviewed.<sup>74</sup> The use of ionic liquids combined with catalysts conducted to much higher 5-HMF yields not only from fructose,<sup>112–118</sup> but also from cheaper carbohydrates such as glucose,<sup>112,113,117–121</sup> sucrose,<sup>117,119,120</sup> inulin,<sup>117,120</sup> starch,<sup>117</sup> cellulose,<sup>112,116,119</sup> and even lignocellulosic materials.<sup>112</sup> In this latter investigation, 1.5 g of corn stover were mixed with 0.75 g of LiCl, 5.63 g of 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), 6.75 g of DMA, 50 mg of CrCl<sub>3</sub>, 26 μL of HCl to obtain a 48% yield to 5-HMF. All these investigations represent a leap forward to increase the yield to 5-HMF from high volume, cheap carbohydrates. However, for a future mass production of 5-HMF, economical and environmental issues should be considered. Carbohydrate processing to 5-HMF is expected to be costly due to the use of ionic liquids, extracting organic agents and catalysts and to the complexity of product recovery and recycling operations. In addition, the simultaneous use of mineral acids, chlorides, chromium compounds, ionic liquids and organic extracting agents throws some doubt on the green character of some investigations. The environmental impact of using non-biodegradable ionic liquids, solvents, and heavy metal chlorides was hardly evoked in most investigations except that Ilgen and coworkers<sup>120</sup> who recognised the needs for ecological and economic assessments.

Alternatively, 5-HMF was prepared from furfural by hydroxymethylation with aqueous formaldehyde in the presence of dealuminated mordenites;<sup>122</sup> a 30% yield was increased up to 50% as an organic co-solvent was used for the extraction of 5-HMF from the aqueous phase. Mascall and Nikitin<sup>123,124</sup> treated glucose, sucrose, or cellulose with hydrochloric acid to obtain 5-(chloromethyl)furfural, which was hydrolysed at 100 °C yielding 86% of 5-HMF and 10% levulinic acid.

**3.1.2 Synthesis of 5-HMF derivatives.** The oxidation of 5-HMF was attempted to synthesise selectively either 2,5-diformylfuran (2,5-DFF) or 2,5-furandicarboxylic acid (2,5-FDCA) (Fig. 2). 2,5-FDCA is a potential substitute for terephthalic or isophthalic acids in the manufacture of polyamides, polyesters and polyurethanes.<sup>100</sup> It was easily synthesised in almost quantitative yield by oxidation with molecular oxygen of 5-HMF in water solution in the presence of carbon or alumina-supported, Pt-catalysts under controlled pH.<sup>125,126</sup> A 98% yield to 2,5-FDCA was obtained by oxidation of 5-HMF with molecular oxygen over Pt/ZrO<sub>2</sub> catalysts.<sup>127,128</sup> Supported gold catalysts were active in 5-HMF oxidation in the presence of a large excess of alkali, but they were subject to deactivation.<sup>129,130</sup> A Au/CeO<sub>2</sub> catalyst afforded a 99% yield to 2,5-FDCA.<sup>130</sup> Oxidation of 5-HMF in methanol solution under oxygen pressure over the Au/TiO<sub>2</sub> catalyst in the presence of sodium methoxide yielded 98% of the methyl ester of 2,5-FDCA.<sup>131</sup> Supported Pt, Pd, and Au catalysts were compared in the aqueous-phase oxidation of 5-HMF to 2,5-FDCA at 295 K.<sup>132</sup> The intermediate reaction product 5-hydroxymethyl-2-furancarboxylic acid (HFCA) was formed in high yield over Au/C and Au/TiO<sub>2</sub> catalysts, but the oxidation did not continue substantially toward 2,5-FDCA; in contrast,

Pt/C catalysts yielded 79% of 2,5-FDCA. A direct conversion of fructose to 2,5-FDCA was attempted with a phase separation system based on membrane technology, but the yield was limited to 25%.<sup>133</sup> Ribeiro and Schuchardt<sup>134</sup> reported that fructose was converted in one-pot reaction to 2,5-FDCA with a 99% selectivity at 72% conversion under air pressure in the presence of cobalt acetylacetonate encapsulated in sol-gel silica.

2,5-Diformylfuran (2,5-DFF) is used in the synthesis of diamine and Schiff bases<sup>100</sup> and finds many other applications.<sup>135</sup> The oxidation of 5-HMF by molecular oxygen in the presence of platinum metals was not selective to 2,5-DFF.<sup>125</sup> Oxidation with hydrogen peroxide on TS1 catalysts afforded a 25% yield.<sup>136</sup> Moreau and coworkers<sup>137</sup> carried out the air oxidation of 5-HMF in toluene and methyl isobutyl ketone in the presence of supported V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts; a 95% selectivity to 2,5-DFF at 90% conversion was reported. 5-HMF was oxidised in air on metal/bromide catalysts, which are used on the industrial scale for the synthesis of terephthalic from *p*-xylene, affording a 57% yield to 2,5-DFF.<sup>138</sup> The aerobic oxidation of 5-HMF was studied over vanadyl complexes immobilised on a PVP polymer and over SBA-15 mesoporous materials in the presence of a pyridine additive; the first catalyst afforded a 99% selectivity at 82% conversion and the second a 98% selectivity at 50% conversion.<sup>139</sup> A 97% selectivity to 2,5-DFF at 84% conversion was obtained in the air oxidation of 5-HMF in the presence of VOPO<sub>4</sub>, 2H<sub>2</sub>O catalyst and *N,N*-dimethylformamide.<sup>140</sup> The aerobic oxidation of 5-HMF in acetonitrile over Cu(NO<sub>3</sub>)<sub>2</sub>/VOSO<sub>4</sub> catalysts yielded 99% of 2,5-DFF.<sup>141</sup> Halliday and coworkers<sup>135</sup> succeeded in achieving a two-step conversion of fructose in DMSO solution without isolation of the 5-HMF intermediate yielding 45% 2,5-DFF; the dehydration and oxidation steps were achieved over an acidic resin and a vanadium catalyst, respectively.

The hydrogenation of 5-HMF was carried out over supported metal catalysts under various reaction conditions.<sup>142</sup> The selectivity was controlled either to 2,5-bis(hydroxymethyl)furan (2,5-BHMF), which is used in the manufacture of polyurethane foams,<sup>143</sup> or to 2,5-bis(hydroxymethyl)tetrahydrofuran, which is used for the manufacture of polyesters.<sup>100</sup> An alternative method of hydrogenation of 5-HMF was achieved using formic acid as a hydrogen donor in the presence of iridium or ruthenium complexes.<sup>144</sup>

2,5-Dimethylfuran (2,5-DMF) was obtained with a 71% yield by vapour phase hydrogenolysis of 10 wt% 5-HMF in 1-butanol solution in a flow reactor loaded with a Cu–Ru/C catalyst.<sup>145</sup> A 95% yield to 2,5-DMF was obtained by heating a solution of 5-HMF in refluxing tetrahydrofuran in the presence of formic acid, H<sub>2</sub>SO<sub>4</sub>, and Pd/C catalyst.<sup>146</sup> The hydrogenation of HMF dissolved in [EMIM]Cl and acetonitrile at 393 K under 62 bar of H<sub>2</sub> pressure over Pd/C resulted in a 32% selectivity to 2,5-DMF at 47% conversion.<sup>121</sup> 2,5-Dimethyltetrahydrofuran was obtained with a 79% yield from fructose by hydrogenation in a H<sub>2</sub>O/toluene/HI mixture in the presence of a RhCl<sub>3</sub> catalyst.<sup>147</sup> In all these investigations, 2,5-DMF and its saturated analogue were targeted as transportation fuels. The value chain leading to these potential fuels would require a complete economic and environmental assessment in view of the overall complexity of the process and weak final yields starting from glucose.

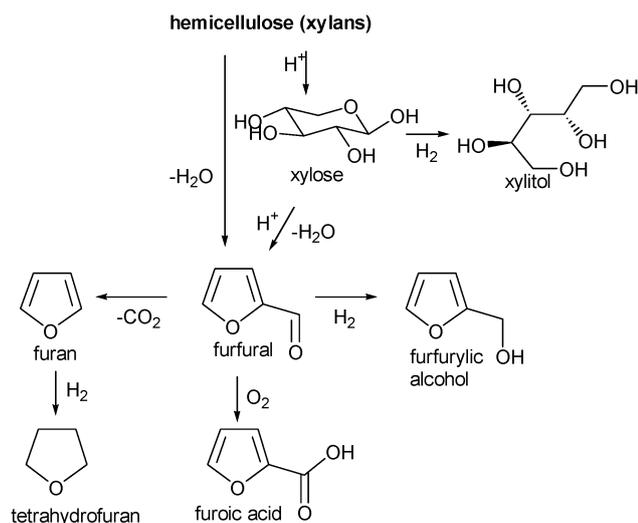


Fig. 3 Xylose, furfural and derivatives.

### 3.2 Xylose and furfural, C<sub>5</sub> platform

The acid catalysed hydrolysis of xylan-type hemicelluloses, present in soft woods and straw, yields C<sub>5</sub> sugars such as xylose, which can be further dehydrated to furfural (Fig. 3). Reviews were published on the chemistry of xylose<sup>148</sup> and furfural.<sup>149</sup>

Xylose was hydrogenated into xylitol, a polyol widely employed as food, cosmetic and pharmaceutical additives. Hydrogenation reactions were mainly achieved industrially in the presence of Raney nickel catalysts affording up to 98% yield, but the catalysts suffered from deactivation due to the leaching of promoters, surface restructuring and poisoning by strongly adsorbed organic molecules.<sup>150,151</sup> A continuous ultrasound irradiation was able to decrease catalyst deactivation.<sup>151</sup> Ru/C catalysts have a higher activity than Raney nickel and are less prone to deactivation.<sup>6</sup> Xylitol yields higher than 98% were reported on Ru/SiO<sub>2</sub> and Ru/ZrO<sub>2</sub> catalysts.<sup>152</sup>

Furfural is produced industrially (*ca.* 250 000 tonnes per year) by hydrolysis of agricultural or forestry wastes with concentrated sulfuric acid.<sup>149,153,154</sup> Interestingly, furfural is the only large-volume, unsaturated chemical produced from carbohydrates. It is employed as a foundry sand linker, in the refining of lubricating oil, and as an intermediate for furfuryl alcohol, furan and tetrahydrofuran production.<sup>155</sup> Many attempts were made to improve the conventional process of xylose cyclodehydration to furfural in H<sub>2</sub>SO<sub>4</sub> solutions. It was shown that metal chloride salts added to acid solutions promote the formation of 1,2-enediol, thus favouring the subsequent acid catalysed dehydration to furfural.<sup>156</sup> Xylose dehydration in acidic solutions was achieved in a biphasic reactor (water/MIBK) yielding up to 85% of furfural.<sup>157</sup> In the presence of β-type zeolites (Si/Al = 12) embedded in a siliceous TUD-1 mesoporous matrix, the furfural yield was 74% at 98% xylose conversion.<sup>158,159</sup> A 46% furfural yield was obtained with the ZSM-5 zeolite and a kinetic model was proposed.<sup>160</sup> A 98% yield was attained over H-mordenite in a biphasic (aqueous/toluene) plug-flow reactor.<sup>161</sup> A one-pot conversion of hemicellulose suspended in water was achieved at 170 °C in the presence of an H-USY catalyst yielding 41% of pentoses (xylose and arabinose) and 12% of furfural.<sup>162</sup>

Furfuryl alcohol is currently manufactured industrially by hydrogenation of furfural in the liquid or vapour phase over copper-chromite catalysts. A number of studies were aimed at finding more environmentally acceptable catalysts than copper-chromite which could selectively hydrogenate the carbonyl group and preserve the C=C bonds. This was not possible over nickel or platinum catalysts unless their surface was modified. Thus, the hydrogenation of furfural over Raney nickel modified by impregnation with heteropolyacid salts, particularly Cu<sub>3/2</sub>PMo<sub>12</sub>O<sub>40</sub>, gave a 96.5% yield to furfurylic alcohol.<sup>163</sup> The vapour phase hydrogenation at 473 K resulted in almost 98% yield over Cu–Co/SiO<sub>2</sub><sup>164</sup> and Cu–MgO<sup>165</sup> catalysts. Bimetallic Pt–Sn catalysts containing different amounts of tin added by controlled surface reactions were used in the liquid-phase hydrogenation of furfural;<sup>166</sup> a 98% selectivity to furfuryl alcohol was attained over Pt–Sn<sub>0.3</sub>. Stevens and coworkers<sup>76</sup> designed a switchable system based on two consecutive fixed-bed flow reactors loaded with copper chromite and Pd/C catalysts, respectively, to achieve the hydrogenation of furfural in supercritical CO<sub>2</sub>; depending on reactor temperatures and H<sub>2</sub>-concentration, furfural was hydrogenated selectively to furfuryl alcohol (97% yield), tetrahydrofurfuryl alcohol (96% yield), 2-methylfuran (90% yield), 2-methyltetrahydrofuran (82% yield), and furan (98% yield).

The vapour-phase decarbonylation of furfural to furan was performed in a fixed-bed reactor at 260 °C on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts loaded with potassium carbonate to promote the decarbonylation and suppress hydrogenation side reaction; with an optimum potassium loading of 8 wt%, a 99.5% yield was obtained.<sup>167</sup> The conversion of furfural to furan was also reported by vapour phase decarbonylation over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts promoted with alkali carbonate which improved the selectivity and catalyst lifetime.<sup>168</sup>

Furoic acid was obtained quantitatively from furfural by oxidation of aqueous solution with molecular oxygen under mild conditions (atmospheric pressure, 65 °C, pH 8) over a 5 wt% Pt/C catalyst promoted with lead.<sup>169</sup> Furfural oxidation with hydrogen peroxide in acidic solutions yielded 2(5H)-furanone which was subsequently reacted with fatty amines to synthesise surfactants.<sup>170</sup> Ketone derivatives were obtained from furfural by aldol condensation.<sup>155</sup> Various hydrogenation products were selectively obtained by hydrogenation of 4-(2-furyl)-3-butene-2-one over ionic liquid-stabilised, ruthenium nanoparticles.<sup>171</sup> Furfural was oxidised by sodium chlorate in the presence of V<sub>2</sub>O<sub>5</sub> into fumaric acid, which was subsequently hydrogenated selectively either to succinic acid or 1,4-butanediol on Pd/C and Pd–Re/C catalysts, respectively;<sup>172</sup> these two monomers were then condensed into poly-(butylene succinate) which is a 100% biomass-based polymer as controlled by measurements of <sup>14</sup>C concentration with an accelerator mass spectrometer (AMS).

### 3.3 Levulinic acid/γ-valerolactone platform

Levulinic acid has been of interest for many years because it can be converted to valuable chemicals (Fig. 4).<sup>173,174</sup> The biofine renewables process was developed at the industrial scale for the production of levulinic acid from cellulose and hemicellulose present in agricultural or forest residues.<sup>175,176</sup>

The raw material was hydrolysed and dehydrated by acidic treatments in a first reactor yielding 5-HMF which was recovered and converted in a second reactor to levulinic acid with a 60% yield with respect to the monomers contained in the starting cellulosic materials. A kinetic study of glucose conversion to levulinic acid in  $\text{H}_2\text{SO}_4$  solutions was performed to study the influence of various reaction parameters.<sup>177</sup>

There are few reports on the use of heterogeneous catalysts for the preparation of levulinic acid. The conversion of glucose on acidic zeolites resulted in a 10% yield to levulinic acid.<sup>178</sup> Solid-supported acid catalysts were active for the hydrolysis at 190 °C of cellulose to glucose and levulinic acid, but only a few percents of levulinic acid were obtained.<sup>179</sup> An alternative route to produce levulinic acid derivatives was achieved by ethanolysis of furfuryl alcohol on acidic resins yielding 87% of ethyl levulinate.<sup>180</sup>

In the past few years attention was highly focussed on  $\gamma$ -valerolactone (GVL) obtained by hydrogenation of levulinic acid (Fig. 4). Horvath and coworkers<sup>181,182</sup> pinpointed the unique physical and chemical properties of GVL which make it an ideal liquid for use as a solvent, intermediate in the chemical industry or for energy storage. Manzer<sup>183</sup> showed that GVL was obtained with a 97% yield by hydrogenation of levulinic acid at 150 °C over a 5 wt% Ru/C catalyst. The hydrogenation process was optimised by achieving a continuous conversion process over a Ru/SiO<sub>2</sub> catalyst in supercritical CO<sub>2</sub> resulting in a 99% yield and the easy separation of GVL from water.<sup>184</sup> Pt/TiO<sub>2</sub> or Pt/ZrO<sub>2</sub> catalysts afforded a continuous hydrogenation of levulinic acid with marginal deactivation over 100 h yielding 95% of GVL.<sup>185</sup>

The direct synthesis of GVL from fructose aqueous solution without isolation of levulinic acid was achieved with a 62% yield in an autoclave pressurised with hydrogen and loaded with water, trifluoroacetic acid and Ru/C catalyst.<sup>186</sup> The hydrogenation of levulinic acid to GVL was also performed using formic acid as a hydrogen donor in the presence of ruthenium catalysts.<sup>187</sup> Leitner and coworkers<sup>188</sup> conducted the hydrogenation of levulinic acid in the presence of ruthenium complexes.

They demonstrated that the selectivity can be tuned to GVL, 1,4-PDO or 2-MTHF depending on the nature of ligands and additives; thus a 95% yield to 1,4-PDO was obtained with the triphos ligand, but upon addition of an acidic ionic liquid the selectivity was shifted to 2-MTHF obtained in 92% yield.

Manzer<sup>174</sup> patented many applications of levulinic acid and derivatives for the synthesis of chemicals, thus 8 patents were issued on the conversion of levulinic acid to pyrrolidones that can be used as solvents and surfactants. The gas phase reaction of GVL with formaldehyde over alkaline hydroxides supported on silica conducted very selectively (>95%) to  $\alpha$ -methylene- $\gamma$ -valerolactone (MGVL), an attractive acrylic monomer that imparts high thermal stability to polymers.<sup>183</sup> Levulinic acid esters were obtained by reaction of  $\alpha$ -angelicalactone with alcohols or with olefins/water in the presence of solid acid resins.<sup>174</sup>

A number of recent applications of levulinic acid derivatives were directed at producing transportation fuels such as pentanoic esters<sup>185,189</sup> and even butenes.<sup>189,190</sup> However, the environmental and economic sustainability of a multi-step value chain going from cellulose to butene *via* levulinic acid and GVL should be addressed.

### 3.4 Sorbitol platform

Sorbitol is produced industrially (*ca.* 700 000 tonnes per year) by catalytic hydrogenation of glucose. Most of the industrial processes rely on batch-wise hydrogenation on Raney nickel catalysts promoted with electropositive metal atoms.<sup>191</sup> Because of the risk of nickel or metal promoter leaching they tend to be replaced by more active and stable supported ruthenium catalysts. Thus, Ru/C catalysts were used in the continuous hydrogenation of glucose in a trickle-bed reactor for up to 596 h on stream yielding 99.5% of sorbitol and experiencing no metal leaching.<sup>192</sup> Hydrogenation of glucose to sorbitol was achieved batch-wise with a 99.5% selectivity to sorbitol at 99.7% conversion on Ru-catalysts supported on activated carbon cloths which were more active than Ru supported on carbon powder and allowed an easy catalyst recycling because no filtration was required.<sup>193</sup> Sorbitol was also obtained in more than 95% yield from starch by a one-pot reaction combining hydrogenation and hydrogenolysis steps on bifunctional Ru-HY catalysts.<sup>194</sup>

Sorbitol finds many applications in food, pharmaceutical and cosmetic industries and as additives in many end-products. It was used as a key intermediate in the synthesis of ascorbic acid (vitamin C),<sup>195</sup> and its fatty acid esters were used as surfactants.<sup>196,197</sup> A new interest arose for isosorbide (1,4:3,6-dianhydro-D-glucitol) obtained by double dehydration of sorbitol.<sup>198</sup> This molecule finds application in pharmaceutical and personal care products and it is used to synthesise polymers, dimethylisosorbide (DMI) or other mono- or di-alkylethers, and isosorbide esters (Fig. 5). The dehydration of sorbitol in the presence of acidic zeolites at 270 °C resulted in a 50% yield to isosorbide.<sup>199</sup> Sulfated copper oxide catalysts afforded a 67% yield to isosorbide at 200 °C.<sup>200</sup> Isosorbide was obtained from cellulose in three successive steps (depolymerisation in  $\text{ZnCl}_2/\text{HCl}$  medium, hydrogenation on Ru/C catalysts and dehydration) without isolation of intermediate products,

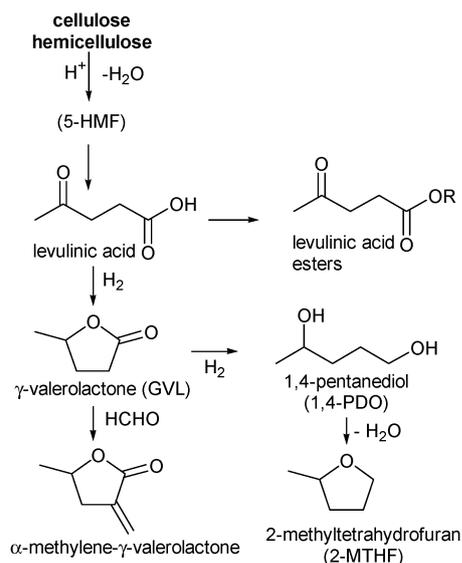


Fig. 4 Levulinic acid and derivatives.

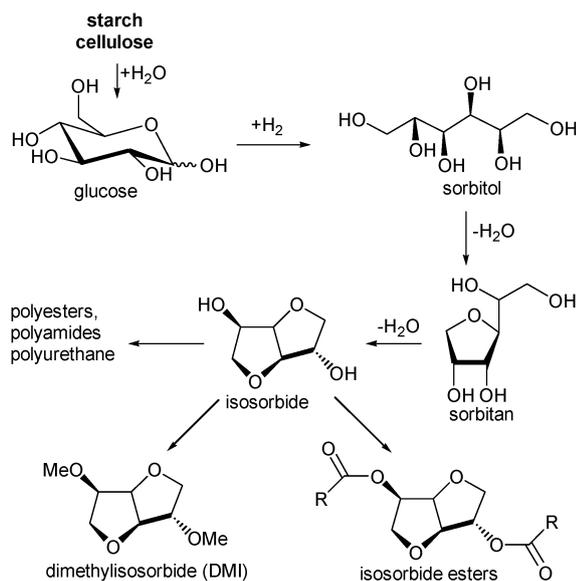


Fig. 5 Sorbitol and derivatives.

however the final yield was not specified.<sup>201</sup> The dehydration of 5 wt% sorbitol solution at 518 K under flowing hydrogen achieved in a continuous fixed-bed reactor loaded with Pt/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts was 100% selective to isosorbide at a conversion lower than 20%.<sup>202</sup>

DMI finds applications in pharmaceutical and cosmetic industries, as a high boiling point solvent which could be used as a substitute for DMSO and DMF, and as a coalescent agent and a solvent in water-borne paints.<sup>203</sup> Roquette Co. patented the use of DMI outside pharmaceutical and cosmetic applications<sup>204</sup> and developed two processes based on isosorbide methylation with CH<sub>3</sub>Cl either in the liquid phase<sup>205</sup> or with gaseous CH<sub>3</sub>Cl affording a 90% yield to DMI.<sup>206</sup> To avoid the use of chlorinated reagents, the methylation of isosorbide was achieved with dimethylcarbonate in the presence of strong liquid bases yielding up to 100% DMI.<sup>207</sup> The synthesis of monoalkyl derivatives of isosorbide resulted in short chain amphiphiles with hydrotropic properties.<sup>208,209</sup> Mono and dialkyl derivatives were also successfully tested for application as a bitumen additive.<sup>210</sup>

Acidic resins have been used in the esterification of isosorbide with *n*-octanoic acid to give the diester in 98% yield.<sup>211</sup> Oligomeric isosorbide esters prepared by reaction of isosorbide with diacids (adipic; dihexanoic) were successfully tested as PVC plasticisers designed to replace phthalates.<sup>212</sup> Isosorbide and other 1,4:3,6-dianhydrohexitols (isomannide, isoidide) are attractive monomers because of their rigidity, chirality, and absence of toxicity; their potential applications in polyesters, polyurethanes and as a substitute for bisphenol-A are promising.<sup>213</sup> Polyethylene terephthalate obtained by co-polymerisation of ethylene glycol and isosorbide with terephthalic acid demonstrates improved mechanical properties.<sup>214</sup>

Isosorbide provides an example of a new product without a synthetic counterpart derived from cheap and widely available polysaccharides *via* very selective catalytic steps following all the principles of green chemistry. Besides its biosourced origin isosorbide and derivatives are attractive products because of

their bio-compatibility and their suitability to fill a number of present and potential applications.

### 3.5 Succinic acid platform

The bulk of succinic acid (SA) production (*ca.* 25 000 tonnes per year) is currently obtained from maleic anhydride produced by oxidation of *n*-butane or butadiene.<sup>215</sup> However, recent advances in fermentation from carbohydrates and purification technologies succeeded in making bio-based succinic acid economically attractive. The economic and environmental analysis of a biorefinery producing succinic acid showed that bio-succinic acid may become a promising intermediate provided that its production cost could be lowered.<sup>216</sup> Three companies, namely MBI,<sup>217</sup> BioAmber<sup>218</sup> and Reverdia,<sup>219</sup> which are a joint venture between DSM and Roquette companies, are currently producing bio-based SA at the pilot or industrial scale. Recent reviews on the catalytic conversion of SA to chemicals have been published,<sup>2,220,221</sup> therefore the present review will focus on recent literature data.

Various chemicals that have a well established market can be produced from the SA platform, such as 1,4-butanediol (BDO),  $\gamma$ -butyrolactone (GBL), tetrahydrofuran (THF), 2-pyrrolidone, *N*-methyl-2-pyrrolidone, and SA esters (Fig. 6). Abundant patent literature was published on the hydrogenation of maleic or succinic anhydride to the three industrial hydrogenation products. Investigations were conducted to understand how catalysts can modify the selectivity towards one of the three hydrogenation products. Deshpande and coworkers<sup>222</sup> showed that GBL, BDO and THF were formed successively, but the product distribution was only partially controlled by tuning the composition of bimetallic ruthenium-cobalt catalysts. The hydrogenation of succinic anhydride to GBL was achieved with a 97% selectivity at 97% conversion on Au/TiO<sub>2</sub> catalysts;<sup>223</sup> the addition of small amounts of platinum favouring H<sub>2</sub> dissociation resulted in higher activities. A 54% yield to GBL was obtained on Pd-catalysts supported on mesoporous aerogels<sup>224</sup> and a correlation was established between the density of acidic sites and the final yield to GBL.<sup>225</sup> Using Pt-group metal catalysts supported on Starbon<sup>®</sup>, a novel mesoporous carbon derived from starch, Luque and coworkers<sup>226</sup> showed that the selectivity to BDO, GBL and THF can be tuned by the proper choice of catalyst; thus Rh/Starbon<sup>®</sup> exhibited a particularly good selectivity to

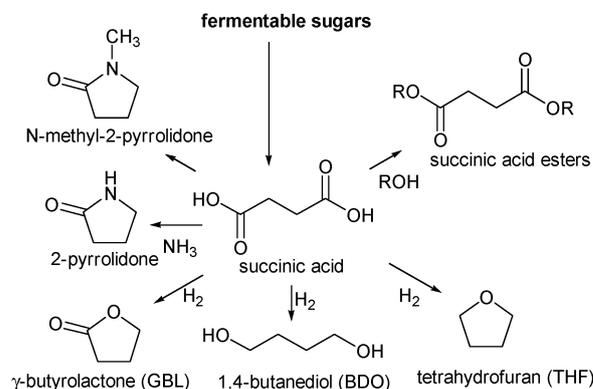


Fig. 6 Succinic acid and derivatives.

BDO (90% selectivity at 60% conversion) while Ru/Starbon<sup>®</sup> was highly selective to THF. It was shown that Ru/Starbon<sup>®</sup> catalysts were more active and selective to THF than Ru/C on conventional carbon supports.<sup>227</sup>

The investigations discussed above were mainly conducted on commercial SA obtained by synthesis from hydrocarbons. To be used as a building block for chemistry, bio-sourced succinate obtained by fermentation should be subjected to various purification technologies to eliminate proteins and organic acids present in fermentation broths. Downstream purification accounts for more than 60% of the total production cost.<sup>221</sup> The most advanced purification techniques such as those based on distillation–crystallisation result in 99% SA purity.<sup>228</sup> Still, the remaining impurities could poison the activity or modify the selectivity of catalysts. Thus the hydrogenation rate of bio-succinic acid over Pd–Re/C catalysts at 160 °C under 150 bar of H<sub>2</sub>-pressure was lower than on synthetic SA (complete conversion at 83 h vs. 46.5 h) and a lower selectivity to BDO (42% vs. 62%) was observed at 75% conversion.<sup>229</sup>

Clark and coworkers<sup>230</sup> showed that acidic Starbon<sup>®</sup> mesoporous materials were 2 to 10 times more active in succinic esterification with ethanol than conventional carbons, this was attributed to different hydrophilic environments and micro-porosity/mesoporosity ratios. The esterification of SA with ethanol was conducted either with pure synthetic SA or bio-sourced SA obtained with different purities from fermentation broths and different downstream purification processes.<sup>231</sup> Whatever the acidic carbons employed, the conversion and selectivity to diester were lower as SA purity decreased; a DRIFT analysis of used catalysts showed that the catalyst surface was covered by organic compounds that could account for catalyst deactivation.

The hydrogenation<sup>229</sup> and esterification<sup>231</sup> studies discussed above show that even after purification succinic acid obtained by fermentation may still contain enough impurities to poison catalyst surfaces and consequently decrease their activity and alter their selectivity. Robust catalysts resistant to deactivation and catalyst reactivation procedures should be developed to convert platform molecules obtained by fermentation of carbohydrates.

The synthesis of 2-pyrrolidone and *N*-methyl-2-pyrrolidone from synthetic SA was essentially described in the patent literature.<sup>2,220</sup> A one-pot synthesis yielding 80% of 2-pyrrolidone was achieved by reacting succinic anhydride and ammonia in water solution at 250 °C under 120 bar pressure in the presence of a Au/TiO<sub>2</sub> catalyst.<sup>223</sup>

### 3.6 Lactic acid platform

Lactic acid (2-hydroxypropanoic acid) has been produced by fermentation of carbohydrates and used in the food industry for a long time and the fermentation and purification technologies were reviewed.<sup>232</sup> Recent improvements of the biotechnological production of enantiomerically pure lactic acid were described.<sup>233</sup> Alternative synthetic routes from glycerol and derivatives were described. Thus, lactic acid and methyl lactate were obtained by conversion of glyceraldehyde and dihydroxyacetone on H-USY zeolites.<sup>234</sup> A direct aerobic oxidation of glycerol on Au–Pt/TiO<sub>2</sub>

catalysts resulted in a 45% yield.<sup>235</sup> A 90% yield to lactic acid was obtained by hydrothermal treatment at 300 °C in water solution containing 0.33 M of glycerol and 1.25 M of KOH.<sup>236</sup> However, these investigations starting from costly pure glycerol could not ensure an economic alternative to fermentation processes.

During the last decade, the interest for lactic acid arose sharply with the development of biodegradable polylactides (PLA) produced by polymerisation of the dilactide derived by self-esterification of lactic acid (Fig. 7). NatureWorks LLC<sup>237</sup> is the main company producing annually a few hundred thousand tons of PLA used mainly in packaging applications. The synthesis and technological development of PLA were described,<sup>238,239</sup> and a recent overview covering every aspect of PLA production, market applications and physico-chemical properties including biodegradability has been published.<sup>240</sup>

Lactic acid is also a building block for the synthesis of chemicals such as acrylic acid, pyruvic acid, 2,3-pentanedione, 1,2-propanediol and lactic acid esters (Fig. 7). A complete literature survey on the conversion of lactic acid to these chemicals has been the subject of a recent review.<sup>241</sup> The dehydration of lactic acid at 598 K on a KI-modified, NaY catalyst yielded 67.9% of acrylic acid at 97.6% conversion.<sup>242</sup> A 58.4% yield to acrylic acid was achieved at 340 °C over a NaY zeolite loaded with 14 wt% of Na<sub>2</sub>HPO<sub>4</sub>.<sup>243</sup> A theoretical study pointed out that an improved selectivity to acrylic acid could be obtained starting from methyl lactate in the presence of sodium polyphosphate catalysts.<sup>244</sup>

Lactic acid was hydrogenated to 1,2-propane diol either in the liquid phase over a Ru/C catalyst,<sup>245</sup> or in the vapor phase over a Cu/SiO<sub>2</sub> catalyst at 473 K affording a 88% yield.<sup>246</sup> A 65% selectivity at 95% conversion was achieved over Cu-catalysts prepared from copper hydroxysilicate catalysts.<sup>247</sup> The effect of residual biogenic impurities present in lactic acid obtained by glucose fermentation on the kinetics of hydrogenation to 1,2-propanediol over Ru/C catalysts was examined;<sup>248</sup> whereas refined lactic acid exhibited a stable conversion, the catalytic activity showed a steep decline with partially refined lactic acid feedstock. Various model impurities were added to pure lactic acid to study the various causes of catalyst deactivation. This illustrates the need for improved fermentation and purification technologies to produce platform molecules with purity suitable for further catalytic processing to chemicals.

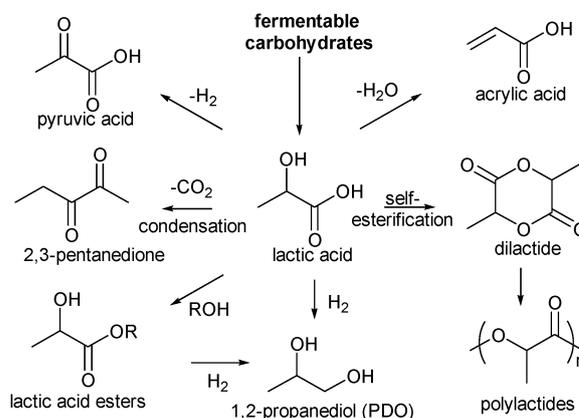


Fig. 7 Lactic acid and derivatives.

## 4. Conversion of biomass to end-products

This section describes a strategy of biomass conversion which is not intended to prepare isolated, pure chemicals that could substitute those obtained from traditional synthesis. Rather it deals with the conversion of biomass in one or few catalytic steps to obtain valuable functional end-products. This approach should decrease dramatically the biomass processing cost which curbs the development of biomass utilisation for bio-product production.<sup>40,41</sup> Typically the starting feedstocks consist of a mixture of homogeneous molecular species such as those present in polysaccharides or vegetable oils which are converted to a mixture of molecules with similar functionalities that can be used without further separation for the manufacture of high tonnage end-products such as paper, paints, resins, foams, lubricants, plasticizers, cosmetics, *etc.* (Fig. 1). This value chain is common in the food processing industry and well-documented in the patent literature, but there are few examples in the Academic literature mostly devoted to multi-step synthesis involving product isolation at each step. Selected examples of conversions of plant oils and polysaccharides are given hereafter to illustrate the potential benefits of a value chain based on more direct conversion of biomass to high tonnage consumer products.

### 4.1 Conversion of triglycerides to oleochemicals

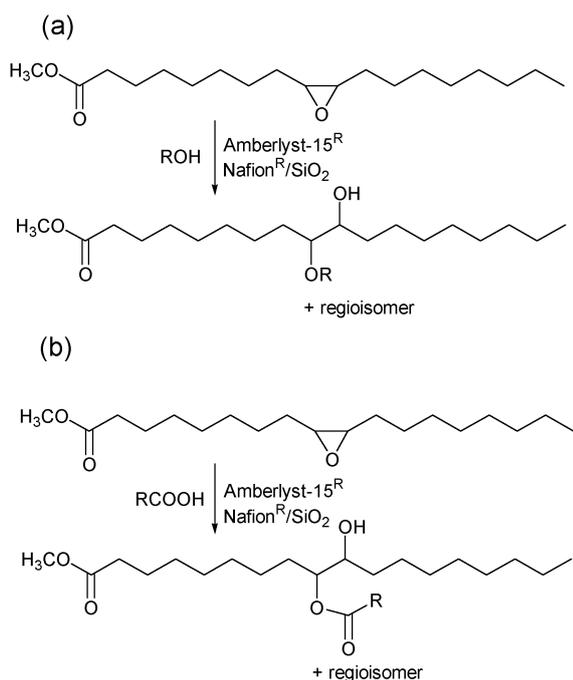
According to Metzger and Meier<sup>249</sup> oils and fats are the most important renewable feedstocks processed in the chemical industry. The annual production of plant oils attains 133 Mega tonnes from which 107 Mega tonnes are employed to cover food needs and the rest is used for bio-diesel production (11 Mega tonnes), and other industrial uses (15 Mega tonnes) including oleochemical production. The development of oleochemicals is limited both by the amount of vegetable oil available for non-food use and by the growing production of biodiesel which is subsidised by government policies.<sup>25,250</sup> Triglycerides (vegetable or plant oils) are glycerol esters of unsaturated fatty acids which differ in chain length ( $C_8$  to  $C_{20}$ ), the position and number of  $C=C$  bonds (0 to 3), and the presence of additional functionalities along the fatty chains. The composition and distribution of fatty acids in triglycerides depend on plant species as well as breeding and genetic modifications.<sup>251</sup> Because of their inherent molecular heterogeneity the conversion of triglycerides results in a mixture of derivatives. Recent reviews have been published on fats and oils as raw materials for the synthesis of industrial products.<sup>2,25,252–256</sup> The synthesis of surfactants containing 100% of renewable carbon and exhibiting a number of desirable properties such as biodegradability, biocompatibility and absence of toxicity is the most successful example of industrial bio-product development. Thus, saccharose or glycerol fatty esters and polyalkylglucosides obtained by acetalisation of fatty alcohols with sugars or polyols constitute high added value surfactants produced in large amounts. Because the reactions leading to the various types of surfactants are well documented, the present review will focus on catalytic reactions involving the  $C=C$  bonds of fatty compounds which are designed to produce lubricants, plasticisers, polyurethanes and new types of polymers.

**4.1.1 Lubricants.** The multi-million tons lubricant market is traditionally based on mineral oils derived from petroleum. Because a large part of them leaks in the environment, regulations have been established in most countries to favour the use of lubricants based on renewable fatty compounds because of their biodegradability and absence of ecotoxicity.<sup>257–259</sup> Unsaturated triglycerides and the corresponding fatty esters obtained by transesterification in the presence of acidic or basic catalysts are well known for their lubricating properties, however they are not stable to oxidation, exhibit a poor cold-flow behaviour and should be modified to meet all specifications such as viscosity or shear stability needed for applications.<sup>259,260</sup> Antioxidant/antiwear additives could be used to improve their properties,<sup>260</sup> however, the lubricating properties of fatty esters were improved by adding new functionalities by reaction with the  $C=C$  bonds.

Various types of oxidation of  $C=C$  bonds were described,<sup>261</sup> but epoxidation followed by aperture of the oxirane ring with alcohols or acids was widely employed. The most common method used in industry to synthesise epoxidised methyl oleate, linoleate, linolenate and commercial soybean oil was the epoxidation of fatty compounds with performic acid generated *in situ* by the reaction of hydrogen peroxide with formic acid.<sup>261</sup> The evaluation of the lubricant properties indicated that epoxidised methyl esters have better stability and friction reducing properties than their methyl ester analogues.<sup>262</sup> Liquid peracids were replaced by oxidising agents such as  $H_2O_2$  or *tert*-butylhydroperoxide (TBHP) in the presence of recyclable acidic heterogeneous catalysts.<sup>263,264</sup> Thus, a 85% selectivity to epoxides at nearly total conversion was obtained in the oxidation of a mixture of sunflower oil methyl esters with TBHP in the presence of Ti-MCM-41 catalysts.<sup>263</sup>

Optimised lubricant properties of epoxidised fatty esters were obtained by oxirane ring opening with alcohols or acids. Thus, the alcoholysis of epoxidised methyl oleate with methanol (Fig. 8a) was achieved with a selectivity higher than 98% in the presence of acidic Amberlyst-15 resin or Nafion<sup>®</sup>/silica composite.<sup>257</sup> Different alcohols were used for the ring opening of epoxidised soybean oil, 2-ethylhexanol resulted in the lowest pour point value.<sup>265</sup> The oxirane ring opening reaction on a mixture of epoxidised methyl esters of rapeseed oil was achieved by the nucleophilic addition of different carboxylic acids (formic, acetic, pivalic, *etc.*) in the presence of various solid acid catalysts (Fig. 8b);<sup>266</sup> high conversions and selectivities were measured with Amberlyst-15 at 30 °C. The evaluation of the lubricant properties of various hydroxy esters demonstrated an improved oxidation stability and viscosity index depending on the length of carbon chain and the nature of carboxylic acid. In a parallel investigation, epoxidised fatty esters were reacted with various carboxylic acids including bio-based levulinic acid,<sup>267</sup> and the lubricant properties of the resulting hydroxy derivatives were fully characterised.<sup>268</sup>

**4.1.2 Plasticisers.** Flexible polyvinyl chloride (PVC) employed in many consumer products contains up to 50 wt% of plasticiser, usually an alkyl phthalate. However, because these compounds are suspected to disrupt human endocrine activity their use is now restricted to toys, food packaging and medical materials.

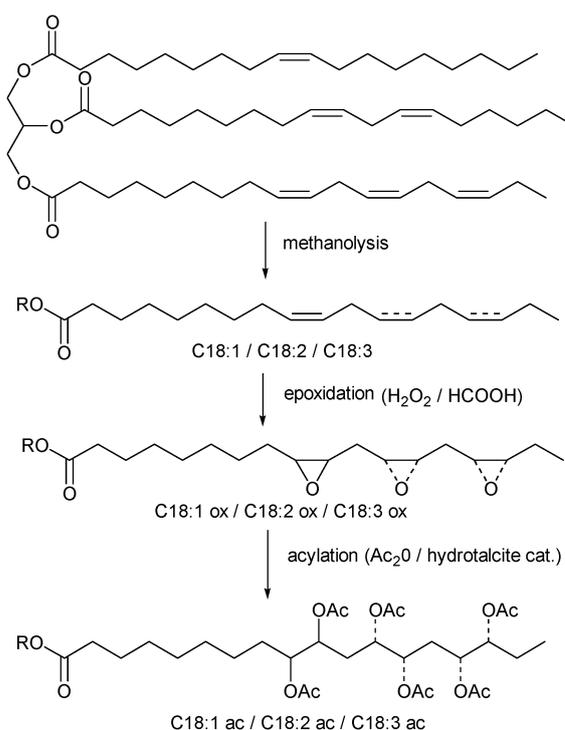


**Fig. 8** Epoxidation of fatty esters and oxirane ring opening (a) with alcohols; (b) with acids.

This prompted the development of alternative plasticisers particularly those prepared from triglycerides.<sup>269,270</sup> Epoxidised vegetable oils (soybean and linseed) is one of the largest industrial applications of vegetable oils with an annual production of about 200 000 tons mainly for use as plasticisers for PVC.<sup>269</sup> Patents have been issued on the synthesis of biocompatible plasticisers obtained from chemically modified castor oil,<sup>271</sup> tall oil obtained from paper pulp processing,<sup>272</sup> and various triglycerides obtained from seed oils.<sup>273</sup>

Recently plasticised PVC was prepared from vegetable oils in three catalytic steps, *viz.*: methanolysis to a mixture of fatty methyl esters, epoxidation of C=C bonds with hydrogen peroxide, and oxirane ring opening with acetic anhydride (Fig. 9).<sup>274</sup> The ring opening of mono, di or tri-substituted epoxides was achieved at 423 K without solvent in the presence of a hydrotalcite catalyst. A 100% yield to the corresponding diacetates was obtained and the solid catalyst was reused four times with constant conversion after a simple regeneration process. The plastisol obtained by mixing the resulting liquid plasticiser with two parts of PVC powder exhibited rheological properties comparable to those of a standard plastisol made from alkyl phthalate.

**4.1.3 Polyurethanes.** Polyurethanes obtained by condensation of polyols and isocyanates constitute a multi-million ton market including flexible and rigid foams, coatings, adhesives, sealants, and elastomers.<sup>275,276</sup> Polyols obtained by oxidation of the unsaturated chains of triglycerides are attractive alternative to petrochemical polyols. Cargill is currently producing polyols from soybean oil (BiOH<sup>®</sup> polyols) that are used for the growing market of flexible foams particularly for home furnitures.<sup>277</sup> Petrovic<sup>276</sup> has extensively studied the manufacture and properties of polyurethanes prepared from polyols obtained by epoxidation/ring opening, ozonolysis and



**Fig. 9** Plasticisers obtained by successive methanolysis, epoxidation and acylation of vegetable oils.<sup>274</sup>

hydroformylation of triglyceride C=C bonds. Polyols obtained by epoxidation/ring opening have only secondary hydroxyl groups shielded by the long fatty acid chains and display lower reactivity than the petrochemical polyols. Ozonolysis combined or not with transesterification was used to increase the number of primary alcohol functionalities.<sup>276,278</sup> The hydroformylation of C=C bonds was used to generate carbonyl groups yielding primary alcohols upon reduction. Thus, the hydroformylation of soybean oil was carried out without solvent in the presence of  $\text{Rh}(\text{CO})_2$ -acac catalysts with triphenylphosphine ligands; the resulting aldehydes were hydrogenated to primary alcohols in the presence of Raney nickel at 110 °C and 7 MPa of  $\text{H}_2$  (Fig. 10).<sup>279</sup>

Undecylenic and oleic acids were used to prepare polyols employed in the synthesis of linear thermoplastic and cross-linked polyurethanes covering a broad range of applications.<sup>280</sup> The biodegradability of vegetable oil-based polyurethanes is limited in cross-linked systems, but higher than in petrochemical-derived polyurethanes.<sup>281</sup> Because polyurethanes may contain residual solvent and even isocyanate monomers, aqueous cationic polyurethane dispersions (PUD) were prepared from methoxylated or epoxidised/acrylated soybean oil to reduce the amount of hazardous volatile organic compounds.<sup>282</sup>

**4.1.4 Polymeric materials.** Triglycerides-based polymers were prepared by free radical, cationic, metathesis and condensation reactions.<sup>283</sup> This fascinating field of investigation, which is out of the scope of the present review, provides many opportunities to produce valuable products that could find application from flexible rubbers to rigid plastics. Particularly, olefin metathesis reactions reviewed by Meier<sup>284-286</sup> provide a powerful tool for the sustainable production of a variety of

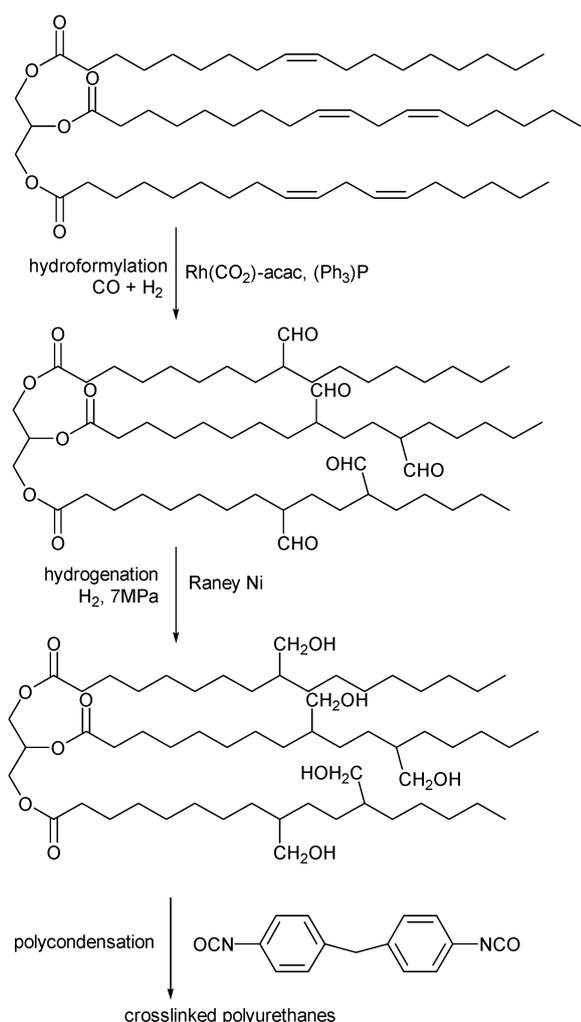


Fig. 10 Conversion of vegetable oils into polyurethanes.

novel polymers from renewable fatty compounds although the industrial applicability is still limited by the high catalyst cost.

## 4.2 Conversion of polysaccharides

Dumesic and coworkers<sup>287,288</sup> demonstrated that aqueous solutions of carbohydrates can be converted in a single hydroprocessing step over PtRe/C catalysts to a mixture of alcohols, ketones, acids, heterocycles, the composition of which was controlled by adjusting process variables. Similarly, a mixture of potentially valuable chemicals was detected in integrated catalytic processing of pyrolysis oils combining hydroprocessing on metal catalysts and conversion on acidic zeolites.<sup>30</sup> However, the mixtures of chemicals formed in these processes were not used for a specific application in chemistry or material science, but were submitted to reduction towards transportation fuels. The present section will focus on the conversion in one or few catalytic steps of polysaccharides or their corresponding monomers to a mixture of chemicals bearing the same functionalities that can be used as such to manufacture end-products.

**4.2.1 Conversion of starch and cellulose.** In an attempt to produce mixtures of polyols suitable for the manufacture of alkyd resins, sorbitol and mannitol aqueous solutions obtained

by combined hydrolysis/hydrogenation of starch hydrolysates on a bifunctional Ru/HY catalyst were partially dehydroxylated on a CuO–ZnO catalyst at 180 °C under H<sub>2</sub>-pressure yielding a mixture of C<sub>4</sub>–C<sub>6</sub> diols, triols and tetrols containing 63% of deoxyhexitols.<sup>289</sup> The copper-based catalysts were chosen to avoid too many C–OH and C–C bond ruptures as it happened with ruthenium catalysts.<sup>290</sup> In the presence of 3 wt% Pd/C catalyst, sorbitol solutions acidified with propionic acid were cyclodehydrated to a mixture of cyclic ethers containing 38% of isosorbide, and 58% of tetrols (2,5-anhydromannitol, 1,4-anhydrosorbitol and 2,5-anhydroiditol).<sup>291</sup> The mixtures of polyols obtained either by dehydroxylation or by dehydration were successfully employed without any further separation or purification to substitute pentaerythritol and other synthetic polyols for the manufacture of polyesters and alkyd resins meeting the specifications required for coating applications.

Most of the current investigations on cellulose aim at deconstructing the biopolymer to produce fermentable sugar and bioethanol. One-pot conversions of cellulose over bifunctional catalysts to sorbitol and other platform molecules such as lactic acid were studied intensively in the past few years.<sup>292–303</sup>

Cellulose was converted into biodegradable alkyl-glycoside surfactants in one-pot transformation carried out in ionic liquid with Amberlyst-15 catalyst;<sup>304</sup> the monosaccharides formed by cellulose hydrolysis reacted with C<sub>4</sub> to C<sub>8</sub> alcohols to give a 82% yield to alkyl- $\alpha,\beta$ -glucosides and alkyl- $\alpha,\beta$ -xylosides.

**4.2.2 Conversion of hemicellulose.** Wheat bran or straw available from agricultural residues are rich in xylan-type hemicellulose built on linear chains of D-xylose which are substituted by 33% of L-arabinose.<sup>148</sup> Hemicelluloses were easily depolymerised by hydrolysis in diluted acid yielding a concentrated wheat bran syrup containing a mixture of pentoses. Because the separation of these compounds would be very costly, the blend of pentoses was used as such to prepare surfactants.<sup>148,305–307</sup> The one-pot conversion of the wheat bran syrup to a mixture of alkyl-pentoside surfactants was achieved by reacting the syrup with *n*-decanol in the presence of diluted sulfuric acid aqueous solution at 90 °C (Fig. 11).<sup>307</sup> The total yield of *n*-decyl-xylosides and *n*-decyl-arabinosides was 63% while the unreacted wheat bran solid residue contained glucan, cellulose, proteins, and lignin. The unpurified mixture of alkyl-pentosides demonstrated good surface tension properties and could be used as a low-cost, non-toxic, biodegradable surfactant suitable for dishwashing and laundry applications.<sup>148</sup>

A mixture of surfactants was also prepared by butadiene telomerisation from a wheat bran syrup containing a mixture of D-xylose and L-arabinose with small amounts of hexose and other pentoses.<sup>148,306,308</sup> Butadiene reacted with the OH groups of polyols in the presence of a soluble palladium catalyst yielding a mixture of mono- and di-octadienyl-xylosides and arabinosides (Fig. 12). The measurements of surface tension indicated that the surfactant properties were equivalent to those of pure octadienyl-pentosides.

A mixture of carboxylic acids that could be used for applications as complexing agents was prepared by one-pot, Fenton-type oxidation of xylan-containing birch wood with H<sub>2</sub>O<sub>2</sub> in the presence of 0.1% FeSO<sub>4</sub> salt.<sup>309</sup>

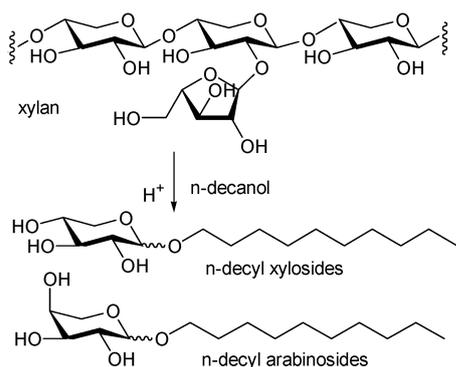


Fig. 11 One pot conversion of wheat bran to alkyl-pentosides.

### 4.3 Conversion of lignin

Lignin accounts for 15 to 30 wt% of woody biomass and it is also available from agricultural residues. The potentialities of this polyphenolic material as a resource for aromatic chemicals were analysed.<sup>310</sup> Lignin was recovered from lignocellulosic materials by kraft pulping, but sulfur-free alternative processes were developed.<sup>62,63,66,311</sup> Many investigations were devoted to depolymerise lignocellulose in an attempt to isolate pure chemicals.<sup>312–316</sup> Thus, lignin was depolymerised by a combination of dealkylation and hydrolysis reactions taking place in water at 623–673 K.<sup>316</sup> Catechol, phenol and cresol were recovered in *ca.* 26, 12, and 11 wt% amount, respectively. The oxidative depolymerisation of lignin in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate with  $Mn(NO_3)_2$  catalyst yielded 11.5 wt% of pure 2,6-dimethoxy-1,4-benzoquinone.<sup>314</sup> The dealkylation of lignin model compounds in ionic liquids in the presence of solid acid catalysts was studied.<sup>317</sup>

The deconstruction of lignin leads to a mixture of aromatic compounds, often in oligomeric form, that can be used as such. Thus, kraft lignin was used to manufacture phenol-formaldehyde binders for wood panels.<sup>318</sup> Sulfur-free organosolv lignins have found several industrial utilisations as material for automotive

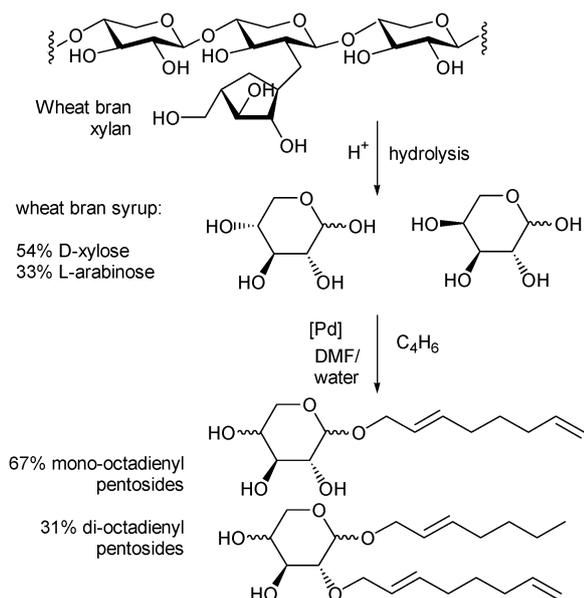


Fig. 12 Butadiene telomerisation of pentoses from wheat bran.

brakes, wood panel products, biodispersants, polyurethane foams, and epoxy resins for printed circuit boards.<sup>319</sup> Cornstalk-derived bio-oils containing oligomers of substituted phenols were used to synthesise phenol formaldehyde resins which fulfilled the specifications of conventional phenol-formaldehyde materials.<sup>320</sup> Abundant patent literature is currently published on the development of lignin conversion processes and on the applications of recovered products.

## 5. Chemical modification of biopolymers

Instead of degrading polysaccharides (cellulose, hemicellulose, starch, inulin, chitin) or other biopolymers (lignin, proteins) into small molecules in an attempt to synthesise chemicals and polymeric materials similar to those currently produced from fossil resources, a more sustainable use of biomass consists of adding functionalities to the biopolymer backbone in one-pot processes to produce functional materials fulfilling various applications. This value chain does not require a number of waste-generating steps and large energy consumption because most conversion processes consist of one-step reaction at moderate temperature, in many instances in water, without further separation processes. This approach was already used 150 years ago to produce cellulose esters and ethers that are still produced today to manufacture coating agents, films and membranes, drilling fluids, explosives, cosmetics, food additives *etc.* The chemical modification of biopolymers is presently a vivid field of research to improve the green character of existing processes and products and to design new chemical modifications leading to innovative marketable end-products. The number of investigations on the subject is exploding as research in polymer science shift to renewable resources. Comprehensive reviews covering the chemical modifications of starch,<sup>321</sup> cellulose,<sup>322–325</sup> hemicellulose<sup>326</sup> and inulin<sup>327</sup> were published. The thriving Academic and patent literature and the numerous product developments at the pilot or industrial scale could not be covered in this review. Instead this section aims at drawing attention on a few illustrative examples of chemical modification of biopolymers which follow green chemistry practices and that are useful for the manufacture of functional products. Attention will be focused on the catalytic modifications of biopolymer functionalities aimed at controlling the hydrophilic/hydrophobic properties of the materials to make them suitable for applications in different high-tonnage end-products. The modifications leading to cationic polysaccharides are also of interest because of their widespread use as flocculents and paper additives. The catalytic modifications of biopolymers are challenging because most of them are in solid, insoluble form, which requires the use of soluble catalysts. The resulting functional groups are grafted on the surface of starch granules or cellulose fibrils, or inside their pores depending on the penetrating ability of reagents and catalysts.

### 5.1 Catalytic modifications increasing hydrophilicity

**5.1.1 Starch.** To meet the specifications required for applications in food, paper and textile industries, the hydrophilic character of starch is often increased by controlled oxidation to generate carbonyl and/or carboxyl functionalities

along the polymer backbone.<sup>328</sup> Industrial processes for starch oxidation have used transition metals salts ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ) as catalysts and mineral oxidising agents such as perchlorates or iodates, thus generating high amounts of wastes. During the last decade, eco-efficient oxidation processes were developed with improved catalytic systems and clean oxidising agents. Starch and other polysaccharides were oxidised selectively at the  $\text{C}_6$  position with the  $\text{NaOCl}/\text{NaBr}$  oxidising system combined with the TEMPO radical (2,2,6,6-tetramethylpiperidine-1-oxyl).<sup>329–331</sup> The oxidation system was made greener by using  $\text{H}_2\text{O}_2$  or  $\text{O}_2$  as oxidising agents and adding an enzyme acting as a co-catalyst.<sup>332</sup> Thus, the primary hydroxyl groups in potato starch were oxidised by the TEMPO mediator using laccase enzyme and oxygen as a primary oxidant.<sup>333</sup>

Potato starch was oxidised with  $\text{H}_2\text{O}_2$  under alkaline and acidic reaction conditions with copper, iron and tungstate catalysts yielding 1.4 carboxyl and 6.6 carbonyl groups per 100 glucose units.<sup>334</sup> Native starch was oxidised in the presence of a water soluble iron-tetrasulphophthalocyanine complex obtained by sulfonation of iron-phthalocyanine which is a cheap industrial blue dye (Fig. 13).<sup>335,336</sup> The hydroxyl groups of anhydroglucose units were oxidised at  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_6$  positions into carbonyl and carboxyl functions. Typically, with a substrate/catalyst ratio of only 25 800/1 the oxidation yielded 1.5 carboxyl and 5.6 carbonyl functions per 100 glucose units. The process was applied to starches obtained from different crops and the resulting materials were successfully tested in the formulation of coating agents and cosmetics. The oxidation mechanism involves a cleavage of the  $\text{C}_2\text{--C}_3$  bond by a nucleophilic iron peroxo phthalocyanine complex as depicted in Fig. 13. Subsequent investigations were conducted to study reaction kinetics<sup>337</sup> in batch mode with ultrasound activation promoting higher degrees of substitution.<sup>338</sup>

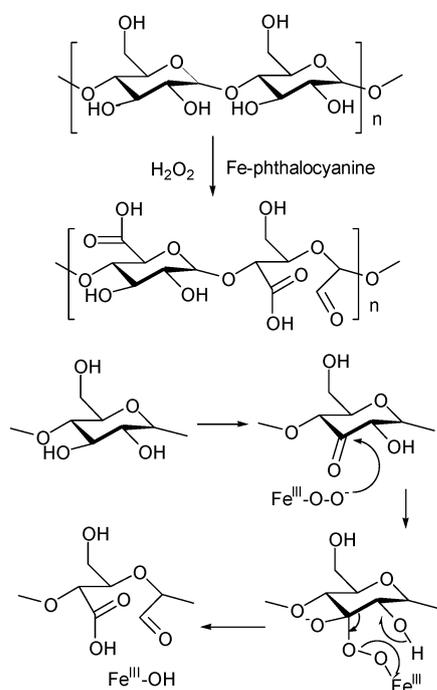


Fig. 13 Starch oxidation catalysed by Fe-phthalocyanine.

High degrees of oxidation were obtained with the  $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2/\text{Br}^-$  oxidation system dissolved in a water-acetic acid mixture, yielding a material acting as a water super-adsorbent, however, the system required high amounts of  $\text{CH}_3\text{ReO}_3$  which have to be regenerated after use because of deactivation.

Starch derivatives containing cationic moieties are important commercial products, used as additives in paper, textile or cosmetic industries. Cationic starch derivatives were prepared by reacting 3-chloro-2-hydroxypropyl-trimethylammonium chloride on starch OH groups yielding water soluble products with high degree of substitution.<sup>339</sup>

**5.1.2 Cellulose and hemicellulose.** The oxidation of cellulose-containing materials was performed with  $\text{NaClO}$  or  $\text{H}_2\text{O}_2$ , with or without metal salts or metal complexes added, for the bleaching of paper pulp and textile.<sup>328</sup> Cellulose oxidation was also achieved to reduce the molecular weight making cellulose more amenable to further transformations, or to generate acidic groups along the biopolymer backbone increasing its hydrophilicity. The TEMPO-mediated oxidation of cellulose at the  $\text{C}_6$  position using  $\text{NaClO}$  as an oxidising agent was extensively studied (Fig. 14).<sup>340–342</sup> Thus, cellulose from bleached kraft pulp was converted to materials employed as transparent gas barrier films for packaging or in high tech applications such as flexible display panels.<sup>340,342</sup> A softwood bleached kraft pulp was subjected to electro-mediated oxidation in water with TEMPO or 4-acetamido-TEMPO without any chlorine-containing oxidant,<sup>343</sup> the oxidation yielded both carboxylic and carbonyl functions at the  $\text{C}_6$  position.

Cellulose, hydroxyethyl cellulose, and carboxymethyl cellulose were oxidised at  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_6$  positions with  $\text{H}_2\text{O}_2$  in the presence of iron-phthalocyanine catalysts.<sup>344</sup> The degrees of substitution (DS) by carboxylic and carbonyl groups were ranging from 15.5 to 5.2 and from 7.2 to 4. These oxidised materials were tested for cosmetic applications.

Galactomannan hemicellulose was oxidised at the  $\text{C}_6$  position of galactose and mannose using the TEMPO/ $\text{NaOCl}/\text{NaBr}$  system yielding a water soluble polymer amenable to easier additional modifications.<sup>345</sup> Etherification of hemicelluloses with cationic agents was used to prepare flocculants, adhesives or wet-end additives in papermaking. Pinel and coworkers<sup>346</sup> achieved the cationisation of galactomannan and xylan hemicelluloses with 2,3-epoxypropyltrimethylammonium chloride in alkaline media resulting in DS values from 0.1 to 1.3 depending on reaction conditions such as the respective hemicellulose and epoxide concentrations.

**5.1.3 Inulin.** Inulin is an oligosaccharide composed of 2 to 60 fructose units connected by  $\beta(2\text{--}1)$  links and terminated by a glucose unit. Water solutions of inulin were oxidised to produce biodegradable polycarboxylates for the sequestration of calcium ions in detergents. Water solutions of inulin were partially (20%) oxidised with  $\text{O}_2$  at the  $\text{C}_6$  position over a Pt/C catalyst resulting in materials meeting various specifications.<sup>347</sup> Using the TEMPO/ $\text{NaOCl}/\text{NaBr}$  oxidation system, a 86% yield to  $\text{C}_6$  oxidised inulin was obtained.<sup>329</sup> Inulin was the subject of many other modifications, notably by esterification and etherification reactions, to produce commercial products

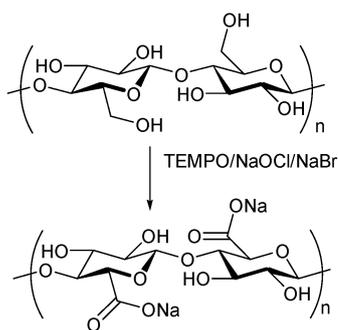


Fig. 14 TEMPO-mediated oxidation of cellulose.

for applications in cosmetics or as drug carriers.<sup>327</sup> Fatty acid esters of inulin were prepared by transesterification of fatty acid methyl esters with inulin in the presence of a basic NaOMe catalyst.<sup>348</sup>

**5.1.4 Chitosan.** Chitosan is a biopolymer obtained by partial deacetylation of chitin, one of the major constituents of the crustacean skeleton and the second most abundant polysaccharide in nature after cellulose. Because of the abundant amino and hydroxyl functional groups along its chain, chitosan can be easily modified. Chitosan has a present and potential wide field of applications because of its antibacterial, chelating and film forming properties. A porous chitosan scaffold prepared by the treatment of chitin whiskers in supercritical CO<sub>2</sub> is a biocompatible, antibacterial matrix well suited for cell culture and living tissue engineering.<sup>349</sup> Nanocomposites of cellulose and chitosan for food packaging, biomedical applications and heavy metal adsorption were easily prepared by minor chemical modifications.<sup>350–352</sup> Chitosan was oxidised with the TEMPO/NaOCl/NaBr system after protection of amine moieties to increase further its hydrophilic properties.<sup>353</sup>

## 5.2 Catalytic modifications increasing hydrophobicity

Starch hydrophobisation is needed to protect it from moisture affecting its mechanical properties or to improve its compatibility with polyethylene in thermoplastic polymer blends.<sup>354</sup> Starch hydrophobicity was increased by esterification with unfriendly stoichiometric reagents such as fatty acid chlorides.<sup>355,356</sup> Pinel and coworkers<sup>357–359</sup> grafted octadienyl chains along starch chains by butadiene telomerisation on the OH groups (Fig. 15). A suspension of insoluble native starch in the water/*i*-PrOH mixture was reacted with butadiene in the presence of a hydro-soluble palladium-catalytic system prepared from palladium diacetate and trisodium tris(*m*-sulfonatophenyl)phosphine. The reaction produced no salt and was 100% atom-efficient. The DS was kept low enough because modified starch should not be too hydrophobic, and for obvious economical reasons the catalyst/starch ratio should be kept low. Modified starch with a DS of 0.06 was obtained with 0.03 wt% palladium at 50 °C; it fulfilled the specifications for use as a thickener for decorative paints. No palladium was detected in the modified polymer when the reaction was conducted in the presence of 0.05% palladium. The process was improved by using a H<sub>2</sub>O–dimethylisorbide or H<sub>2</sub>O–isopropanol solvent and a [( $\pi$ -allyl)Pd(TPPTS)<sub>2</sub>]Cl catalytic system.<sup>358</sup> A further improvement was achieved by conducting the reaction in pure water medium by adding small

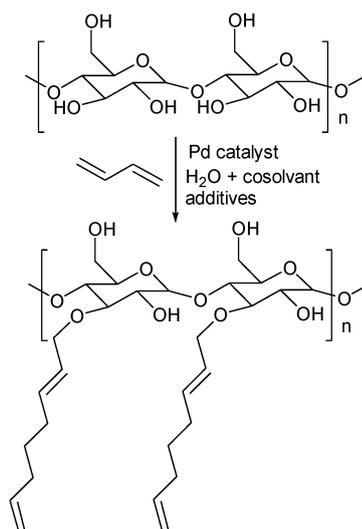


Fig. 15 Hydrophobisation of starch by butadiene telomerisation.

amounts of a cationic surfactant to achieve a good dispersion of butadiene micelles in water and improve their contact with starch granules.<sup>359</sup>

Hydrophobic celluloses were prepared by esterification, fluorination or silylation of surface OH groups with stoichiometric reagents.<sup>324</sup> Water repellent cellulose fibers were obtained by transesterification of soybean oil with cellulose.<sup>360</sup> Hydrophobic materials were prepared by grafting limonene and myrcene on cellulose fibers in a solvent-free process at room temperature involving plasma technology.<sup>361</sup>

The hydrophilicity of hemicelluloses should be decreased to make biodegradable films and coatings designed for food packaging, biomedical and coating industries. The hydrophobisation of hemicelluloses was achieved by esterification with acyl chlorides, fatty acids grafting, or various other methods.<sup>354</sup> Thus, to produce oxygen barrier films for food packaging applications with a low moisture sensitivity, *O*-acetylgalactomannan in water was reacted with benzyl chloride in the presence of a phase transfer catalyst.<sup>362</sup>

The hydrophobisation of chitosan was achieved either by grafting hydrophobic chains by amidation of chitosan with carboxylic acids (Fig. 16),<sup>363,364</sup> or by N-alkylation of chitosan with alkyl bromide.<sup>365</sup> However, the amino group should be preserved to keep the biocide activity of chitosan which requires that hydrophobic chains be grafted by esterification or etherification reactions with the OH groups. Thus, a water resistant, antimicrobial chitosan for paper coating in food packaging was prepared by esterification of the OH groups at C<sub>3</sub> and C<sub>6</sub> positions with palmitoyl chloride.<sup>366</sup> Hydrophobisation was also achieved by silylation of the OH groups after protection of the amino functions.<sup>367</sup>

## 6. Concluding remarks and prospects

### 6.1 Oleochemicals vs. biodiesel

The development of biomass utilisation for industrial applications should not be done at the detriment of food needs. Because the huge amounts of renewable carbon are needed for the manufacture of biofuels they should imperatively be

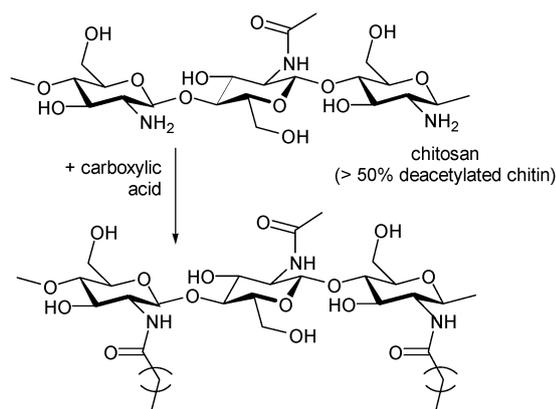


Fig. 16 Amidation of chitosan.

produced from lignocellulosic materials, organic wastes, or any biomass not involved in food chains. This is not yet achieved industrially *e.g.*, for biodiesel production which still relies on triglycerides from edible seed oils. Non-edible oil which can be recovered from plants growing on marginal land such as *Jatropha curcas* or from oil-rich microalgae grown from aquaculture could become a significant alternative for edible seed oils if they are available in sufficient amounts at economic price, but in the meantime the volume of vegetable oils available to manufacture oleochemicals is limited as biodiesel production and food needs are increasing. Oleochemical manufacturers complain that the development of biodegradable surfactants and lubricants is hampered by the growing production of biodiesel which is subsidised by government policies.<sup>25,250</sup>

## 6.2 Biomass conversion and process economy

The development of bioproducts at a large industrial scale requires that their quality and cost meet consumer demand. The final cost of bioproducts includes the price of the starting feedstock, but it also depends heavily upon the processing cost. The latter may be decreased by reducing the number of synthesis steps and improving their yields, but a judicious choice of biomass conversion strategy could be essential to achieve a cost-effective development of biomass utilisation towards bioproducts.

During the last decade the main strategy envisioned to produce chemicals from biomass was deeply influenced by the 2004 US DOE report<sup>80</sup> pointing out “Top 10 chemicals” that could be used as platform molecules for further chemical syntheses. This approach was highly publicised, propelled many Academic investigations and triggered R&D in small and large industrial companies. This is a target-driven approach aiming at producing pure isolated chemicals, usually those with an existing market. Except that it starts from oxygenates, the methodology is close to the traditional multi-step synthesis from hydrocarbons to final products. However, the value chain faces the risk of producing chemicals that are not cost competitive with their petroleum-derived counterparts. The economy depends both on the cost of the platform molecules that have to be produced with enough purity from raw biomass by a combination of extraction, depolymerisation and fermentation processes and on the development of new synthetic pathways

from oxygenated platform molecules that have to be optimised. The cost associated with the purification of platform molecules, particularly those obtained by fermentation or by depolymerisation of lignocellulosic materials could impact severely the overall process economy. Interestingly, the platform molecule value chain was economically successful for the industrial manufacture of bioproducts that have no synthetic counterparts such as isosorbide, alkylpolyglucoside surfactants or PLA polymers.

In the future the platform molecule value chain could become more and more successful to produce high tonnages of bioproducts, but in the meantime most of the high tonnage industrial bioproducts are produced by a different strategy which does not aim at producing pure isolated chemicals competing with those derived from petroleum. This strategy consists of converting biomass in minimum steps to functional products such as surfactants, lubricants, plasticisers, polymers, paper additives, binders, paints, food additives, and cosmetics.<sup>40,41</sup> Many examples illustrating this approach are given in Sections 4 and 5 of this review. As practised in the food industry, it is not always needed to isolate pure chemicals to make marketable products. This value chain is more likely to be cost-competitive because it reduces drastically the number of conversion, extraction and purification steps. One can expect an expansion of this value chain in the domain of polymer science and technology where a large number of petroleum derived polymers could be advantageously replaced by chemically modified biopolymers. The simple, one-pot modification of biopolymers such as polysaccharides, lignin or proteins to functional polymers meeting consumer demand should be more sustainable from both economic and environmental standpoints than the multi-step value chain consisting of degrading biopolymers to small molecules that could serve as monomers such as ethylene or propylene to reconstruct polymers. A complete change of strategy could accelerate greatly the industrial development of chemicals and materials based on renewable carbon.

## 6.3 Biomass conversion and green chemistry

The use of renewable carbon fulfills one of the green chemistry principles, but not necessarily the others. The present literature survey indicates that the benefits for green chemistry are very contrasting depending upon feedstocks, processes and products. Processes requiring too many conversion and separation steps affect the overall atom economy, energy demand and waste emissions. The proportion of renewable carbon in final products is also liable to decrease with the number of synthesis steps. Because of the inhomogeneous composition of renewables and because other impurities are potentially added during fermentation steps, clean and energy efficient separation and purification technologies are of primary importance. Biomass conversion processes achieved in one or few steps without separation of intermediates as described in Sections 4 and 5 of this review are certainly more performing in terms of biomass utilisation and waste minimisation than the more traditional approach *via* platform molecules.

There are a number of examples in the literature of biomass conversion fulfilling nicely all green chemistry principles. Thus, the conversion of starch to isosorbide *via* glucose and sorbitol or the aerobic oxidation of glucose could be achieved

with 100% atom economy in aqueous solutions over heterogeneous catalysts that can be recycled many times. On the other hand the green character of some biomass conversion processes is impaired by the use of toxic reagents and solvents, generates a lot of waste and has a modest atom economy. The sustainability of biomass conversion processes can be evaluated by life cycle analysis (LCA) with a cradle-to-grave or cradle-to-gate approach which requires the inventory and environmental impact assessment of all inputs and outputs of the production system, but this cumbersome approach is hardly operational to assess the multitude of raw materials, processes and chemicals involved in biomass conversion. One would like to rely on simple metrics such as those based on *E*-factor and atom efficiency that could be used as a decision-making tool at an early stage of product synthesis, but as outlined by Sheldon,<sup>368</sup> meaningful metrics for assessing the sustainability of biomass conversion need to be developed.

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