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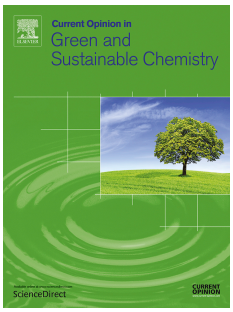

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Chemicals from Renewable Biomass: a Renaissance in Carbohydrate Chemistry

Roger A. Sheldon

Abstract

The conversion of sugars, derived from waste polysaccharide biomass, to commodity chemicals by fermentation or catalytic hydrogenation, oxidation or dehydration or combinations thereof are reviewed.

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Introduction

The origins of the petrochemical industry date back to the 1920s when simple organic chemicals, such as ethanol and isopropanol were first prepared on an industrial scale from byproducts (ethylene and propylene) of oil refining. Its heyday was in the 1960s and it is currently undergoing a transition to more sustainable, carbon neutral manufacture from renewable biomass. This could involve the use of first generation biomass, such as corn starch in the short term [1], but in the long term conversion of waste polysaccharides, available from agricultural residues, is envisaged [2]. Both scenarios involve a switch from hydrocarbons to carbohydrates as basic chemicals. Many commodity chemicals are 'oxygenates', produced by oxidation or hydration of hydrocarbons. In contrast, production from carbohydrates by, for example, catalytic oxidation [3] or reduction[4] is more redox efficient and can be performed in aqueous media. Hence, the recent emergence of biorefineries is leading to a renaissance in carbohydrate chemistry.

Major sources of waste biomass are agricultural residues comprising mainly lignocellulose and pectin (see Figure 1 for structures). On an industrial scale the polysaccharides are converted by enzymatic

hydrolysis to their constituent hexoses and pentoses [2]. In order to be sustainable subsequent processing must be based on green catalytic reactions [5] and, for commercial impact, the products should be large volume commodity chemicals such as industrial monomers.

Figure 1. Structures of the building blocks of polysaccharides

Fermentation processes

Advances in metabolic pathway engineering [6,7], have enabled the cost-effective fermentation of biomass derived sugars to an increasing number of commodity chemicals [8,9]. The challenges involved in achieving commercial viability – molar yield, titre (g/L) and volumetric productivity (g/L/h) – and other considerations, such as byproduct profile and strain robustness, have been reviewed [10]. Since feedstock costs represent a large fraction of total costs (as do hydrocarbon feedstocks in petrochemical refineries), the molar yield should be at least 80%. The product titre determines the downstream processing costs and 50g/L, well above the tolerance limit of many microbes, is considered a minimum. Volumetric productivities dictate reactor size and, hence, capital investment and < 2.0 g/L/h is considered insufficient.

Bioethanol, with a global production of 92 million tonnes in 2014 [11], is the largest volume chemical produced by fermentation and substantial amounts of bioethylene are currently produced by dehydration of bioethanol. Consequently, one scenario for chemicals manufacture is based on bioethylene [12]. Commercialization of microbial production of other lower alcohols - bio-1-butanol [13] and bio-isobutanol [14] as biofuels and commodity chemicals is imminent (Figure 2). Alternatively, energy intensive separation of water miscible lower alcohols can be circumvented by producing olefins, e.g. isobutene [15], directly. Similarly, isoprene [16,17] and the terpene, β-farnesene, with applications ranging from cosmetics to jet fuel, can be produced directly by fermentation [18]. Microbial synthesis

of toluene was recently reported [19], potentially enabling fermentative production of aromatic hydrocarbons.

Figure 2. Production of commodity chemicals by fermentation.

The commercially important diols: 1,3-propanediol (1,3-PDO), 2,3-butanediol (2,3-BDO) and 1,4-butanediol (1,4-BDO) can be produced efficiently by fermentation (Figure2) [20]. Indeed, the development by DuPont [21] of cost-effective production of 1,3-PDO, the key raw material for polytrimethylene terephthalate, in recombinant *E.coli* , was a watershed in modern biotechnology [22].

The next level of sophistication is to construct entirely new pathways as exemplified by the Genomatica process for the industrial monomer 1,4-butanediol (titre >120 g/L and STY 3 g/L/h) by fermentation of an engineered *E.coli* strain [23]. CO_2 emissions and energy usage are 83% and 67% lower, respectively, compared to the petrochemical process. It necessitated the identification, construction and optimization of an entirely new biosynthetic pathway heterologously expressed in *E.coli* cells with increased tolerance to BDO at more than 100 g/L [24].

A variety of carboxylic acids are produced efficiently by fermentation (Figure 2). Lactic acid fermentation, for example, is more cost-effective than the chemical process [25] and global production has significantly increased recently in response to the rapidly increasing demand for biodegradable poly-lactate (PLA) as a green and sustainable alternative to petroleum-derived plastics. Other examples,traditionally produced by fermentation, are citric and gluconic acids [26], more recently joined by itaconic acid [27], the raw material for a variety of renewable polyesters [28] and potentially a precursor of biomethacrylic acid via decarboxylation [29]. Similarly, succinic acid [30] has potentially large volume polymer applications and its microbial production has been implemented by several companies. Further examples of important industrial monomers are acrylic and adipic acids. 3-

hydroxypropionic acid (3-HPA) can be produced by fermentation [31] and dehydrated to acrylic acid and several companies are actively pursuing microbial routes to adipic acid [32].

Catalytic oxidation of carbohydrates

Glucaric acid is a potentially interesting monomer for biodegradable polyamides. The market is currently underdeveloped owing to its limited availability and high price but a Johnson Matthey-Rennovia joint venture is developing the heterogeneous catalytic aerobic oxidation of glucose to glucaric acid and subsequent hydrogenolysis to bioadipic acid (Figure 3)[33].

Figure 3. Conversion of glucose to glucaric and adipic acids

Catalytic hydrogenation of carbohydrates

Catalytic hydrogenation of C_6 and C_5 sugars derived from lignocellulose affords the corresponding hexitols (Figure 4) [34] but ethylene glycol (EG) and propylene glycol (1,2-PG), with global productions of 23 and 2 mio tons per annum, respectively, are more commercially attractive targets. Conversion of glucose to EG and 1,2-PG involves carbon-carbon bond scission via retro-aldol condensations (RACs) catalyzed by, *inter alia*, tungsten-based catalysts (Figure 4). Yields of up to 72-76 % EG, together with small amounts of 1,2-PG, are obtained by hydrogenation of glucose over a Ni-W carbide-on charcoal catalyst [35]. In contrast, Cu-W or Pd-W based catalysts afford 1,2-PG in yields up to 61%, via initial isomerization to fructose followed by RAC to two C_3 units.

Figure 4. Catalytic hydrogenation of C_6 and C_5 sugars

Acid-catalyzed dehydration of carbohydrates to furan derivatives.

Acid catalyzed dehydration of C_5 and C_6 sugars produces furfural and 5-hydroxymethylfurfural (HMF), respectively. Furfural is already an important commodity chemical and HMF has potential [36,37] but its cost-effective industrial production is challenging. It involves initial isomerization to D-fructose and

subsequent acid catalyzed dehydration (Figure 5). Consecutive, acid catalyzed rehydration affords a 1:1 mixture of levulinic acid (LA) and formic acid and polymerization reactions lead to the formation of insoluble polymers (humins) [38]. Use of a water / γ-valerolactone (GVL) biphasic system to continually remove the sensitive HMF from the aqueous phase afforded a maximum yield of HMF from glucose of 62% together with 18% LA [39]. Conducting the reaction in an alcohol affords more stable HMF ethers but it is not clear that this gives higher yields [40].

Figure 5. Acid catalyzed dehydration of glucose to HMF .

2,5-Furan dicarboxylic acid and polyethylene furandicarboxylate (PEF)

The potentially most important product from renewable biomass is undoubtedly polyethylene furandicarboxylate (PEF), a substitute for fossil-based polyethylene terephthalate (PET). PEF is being commercialized by Synvina, a joint venture of Avantium and BASF [41], and Corbion [42] while Dupont is developing the polymer derived from FDCA and 1,3-PDO [42]. A cradle-to-grave comparison [43] of corn-based PEF with fossil-based PET showed that non-renewable energy use would be reduced by 40 - 50% and greenhouse gas (GHG) emissions by 45-55%. Further reduction of the latter would result from a switch to waste lignocellulose as feedstock. Furthermore, PEF has superior mechanical, thermal and gas barrier properties to PET [44]. The key raw material, furan-2,5-dicarboxylic acid (FDCA), is produced by selective aerobic oxidation [45] of HMF using noble metal catalysts [46,47,48,49], free enzymes [50,51] or whole cell biocatalysts [52] in aqueous media (Figure 6).

Figure 6. Routes to FDCA by catalytic aerobic oxidation

The weakest link in the chain is HMF production and the search for alternative methods continues. One possibility is via acid catalyzed dehydration of aldaric acids [53], produced by gold catalyzed aerobic oxidation of uronic acids (Figure 6) [54], e.g. D-galacturonic acid derived from the pectin in sugar beet pulp [55]. Alternatively, isomerization to the corresponding 5-keto aldonic acid followed by acid

catalyzed cyclodehydration in methanol affords the methyl ester of 5-formyl-2-furoic acid that is oxidized to FDCA dimethyl ester in an overall (unoptimized) yield of 45% [56].

Conclusion

The use of renewable polysaccharide feedstocks for biofuels and commodity chemicals has stimulated a revival in carbohydrate chemistry employing green and sustainable chemocatalytic and biocatalytic processes. The flagship example is the synthesis of the new bioplastic, PEF, via FDCA as the platform chemical. We expect that this and other examples will lead to a further proliferation of biobased manufacture of commodity chemicals in the future.

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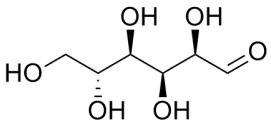

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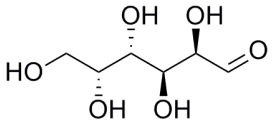

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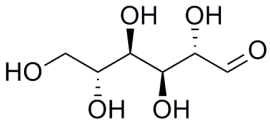

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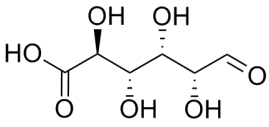

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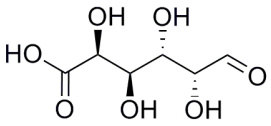

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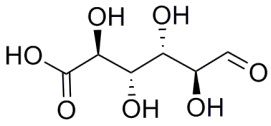

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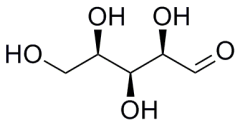

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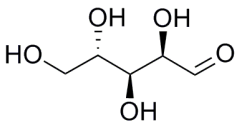

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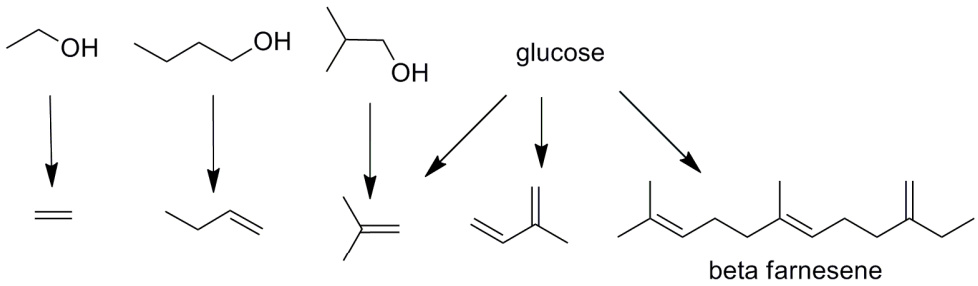

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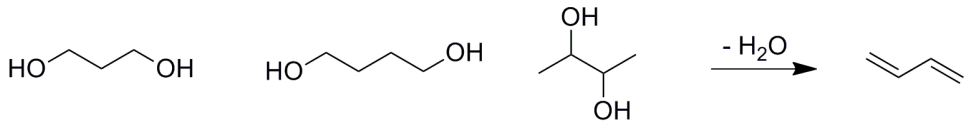
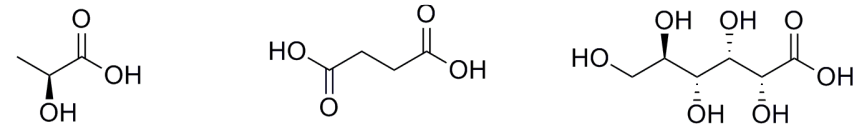
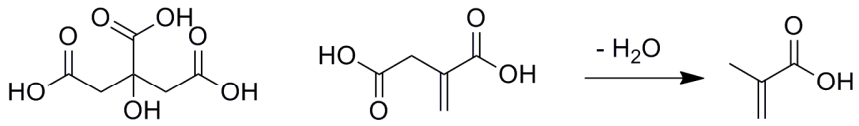
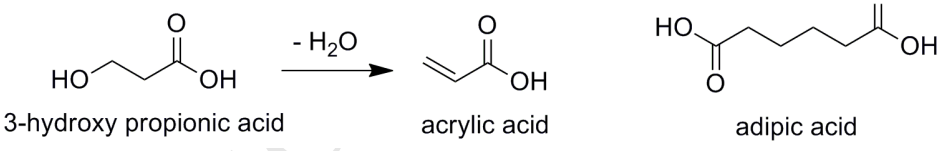
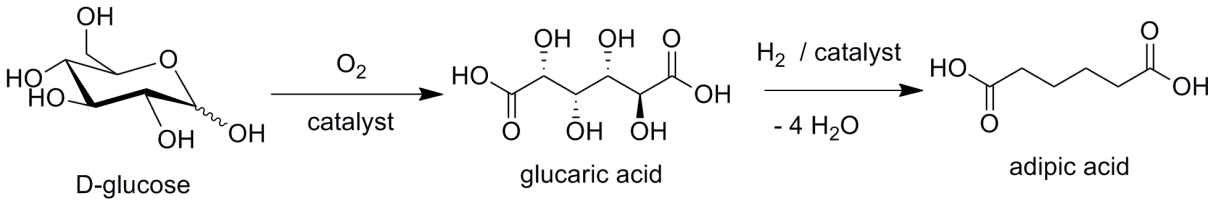


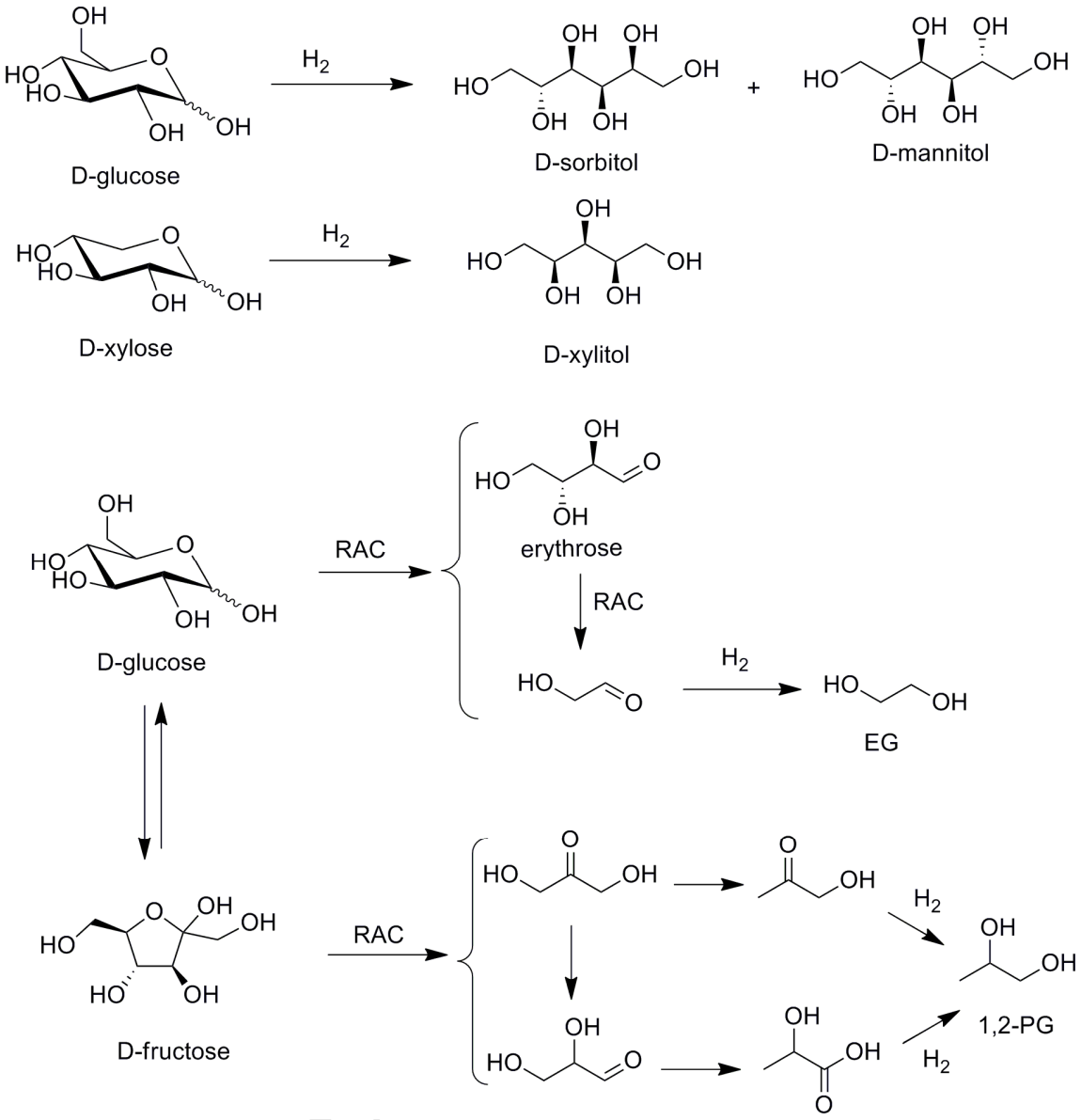
Carboxylic acids

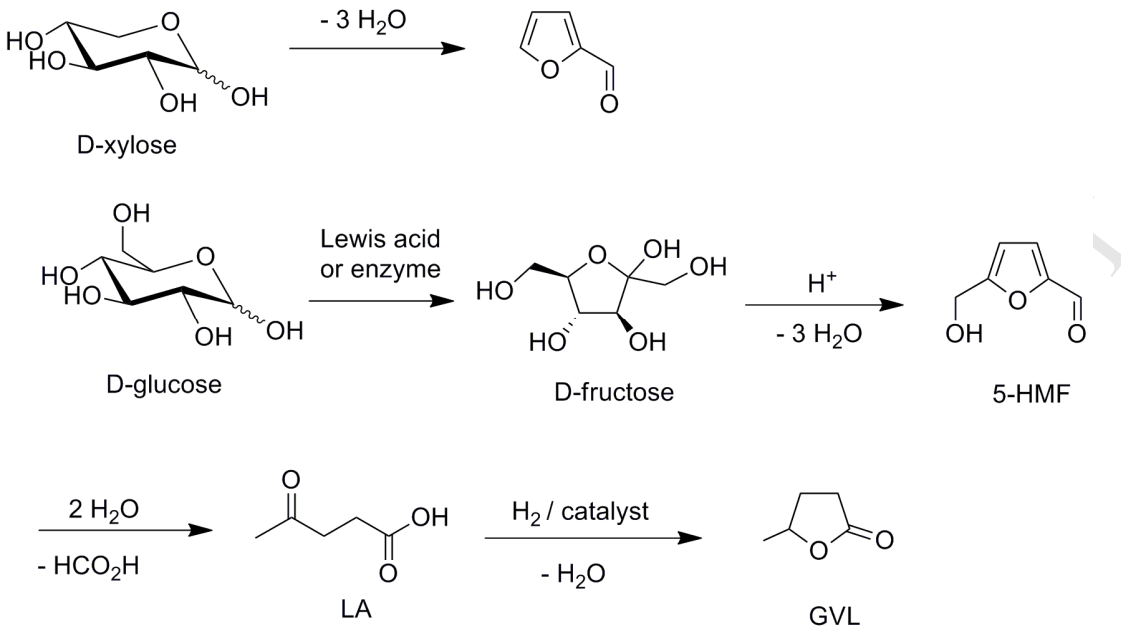




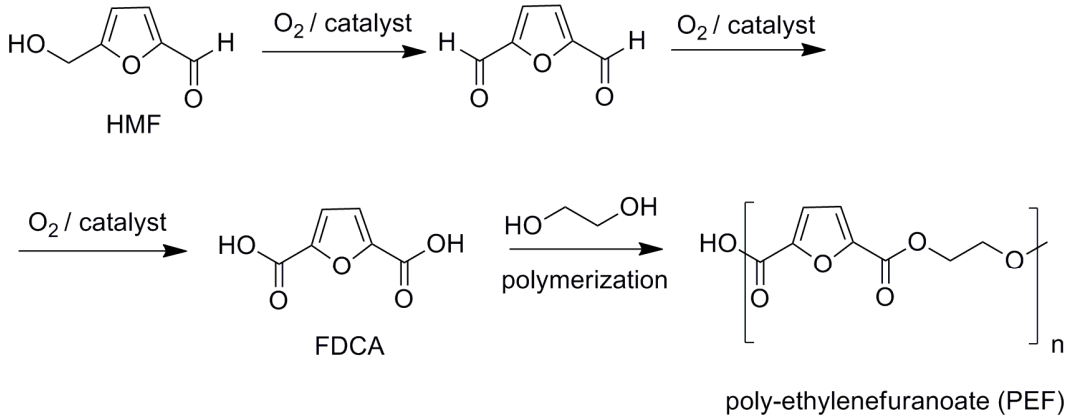





D-glucose
H2
D-sorbitol
+
D-mannitol
D-xylose
H2
D-xylitol
D-glucose
RAC
erythrose
RAC
H2
EG
D-fructose
RAC
H2
1,2-PG
H2



HMF route



Aldaric acid routes