INDUSTRIAL CHEMICALS FROM CARBOHYDRATE FEEDSTOCKS: CURRENT STATUS AND CHALLENGES AHEAD

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1. SUMMARY

In view of the impending transition of chemical industry from depleting fossil raw materials to renewable feedstocks – the end of cheap oil is predicted from 2040-2050 – this account gives an overview on chemically and enzymatically transforming low-molecular weight carbohydrates into products with versatile industrial application profiles which have the potential to replace those presently derived from petrochemical sources.

2. INTRODUCTION

Our health and daily lives rely largely on man-made substances that are produced in a step-by-step process from inexpensive fossil resources – coal, oil, natural gas – and biomass-based feedstocks, yet the extent to which they were used as raw material for the chemical industry has undergone drastic changes over the last 150 years. At the outset, the raw materials basis was substantially renewable (Fig. 1) with the utilization of biomass and coal being in equal about a 100 years ago (Umbach 1996). In the 1920’s, coal tar-based materials took the lead reaching a maximum around 1930, whereas after fossil gas and oil irresistibly took over, eliminating coal nearly completely and reducing renewable feedstocks to very modest levels, presently about 5% such, that presently they have only a 5% share in the total production (DOE 2002).
As our fossil raw materials are irrevocably decreasing and as the pressure on our environment is building up, the progressive changeover of chemical industry to renewable feedstocks for their raw materials emerges as an inevitable necessity (Klass 1998, Okkerse 1999, Bozell 2001, DOE 2002, 2004, Lichtenthaler 2004, 2006), i.e. it will have to increasingly resort to the raw materials basis that prevailed before natural gas and oil outpaced all other sources (cf. Fig. 1). The crucial question today is not “When will fossil fuels be exhausted?” but rather “When will fossil raw materials have become so expensive that biofeedstocks are an economically competitive alternative?” Experts realistically predict the end of cheap oil for 2040-2050 (Campbell 1999, Hiller 2000), a development that we can witness by now already; as chemical industry combats the rising costs of natural oil and gas. Thus, taking this prognostication for the end of cheap oil, the curve for the utilization of biofeedstocks in Figure 1 will have to rise such that it meets that of fossil raw materials somewhere after 2040.

The transition to a more bio-based production system is pressing, yet hampered by a variety of obstacles: Fossil raw materials are more economic at present, and the process technology for their conversion into organic chemicals is exceedingly well developed and basically different from that required for transforming carbohydrates into products with industrial application profiles. This situation originates from the inherently different chemical structures of the two types of raw materials, as terrestrial biomass is considerably more complex, constituting a multifaceted array of low and high molecular weight products, exemplified by sugars, hydroxy and amino acids, lipids, and biopolymers such as cellulose, hemicelluloses, chitin, starch, lignin, and proteins. By far the most important class of organic compounds in terms of volume produced are carbohydrates as they represent roughly 75% of the annually renewable biomass of about 180 bill. tons. Of these, only a minor fraction (ca. 4%) is used by man, the rest decays and recycles along natural pathways.
Thus, carbohydrates, a single class of natural products – aside from their traditional uses for food, lumber, paper, and heat – are the major biofeedstocks from which to develop industrially and economically viable organic chemicals that are to replace those derived from petrochemical sources.

The bulk of the annually renewable carbohydrate biomass are polysaccharides, yet their non-food utilization is confined to textile, paper, and coating industries, either as such or in the form of simple esters and ethers. Organic commodity chemicals, however, are usually of low molecular weight, so they are more expediently obtained from low molecular weight carbohydrates, i.e. from the constituent units of these polysaccharides (Table 1): glucose (cellulose, starch), fructose (inulin), xylose (hemicelluloses), or disaccharide versions thereof, most notably sucrose, are the actual carbohydrate raw materials for organic chemicals with tailor-made industrial applications; they are inexpensive, ton-scale accessible, and provide an ensuing chemistry better worked out and more variable than that of their polymers.

Table 1. The key sugars of biomass: Annual production volume and prices

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Raw Material</th>
<th>World Production (tons/year)</th>
<th>Price (€/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>Sugar cane / beet</td>
<td>140 000 000</td>
<td>0.20</td>
</tr>
<tr>
<td>Glucose</td>
<td>Starch, Cellulose</td>
<td>30 000</td>
<td>0.30</td>
</tr>
<tr>
<td>Fructose</td>
<td>Inulin, Glucose</td>
<td>60 000</td>
<td>1.00</td>
</tr>
<tr>
<td>Xylose</td>
<td>Hemicelluloses</td>
<td>15 000</td>
<td>3.50</td>
</tr>
<tr>
<td>(Glucosamine</td>
<td>Chitin</td>
<td>?</td>
<td>200.--</td>
</tr>
</tbody>
</table>
3. PRESENT NON-FOOD INDUSTRIAL USES OF SUGARS

The present utilization of carbohydrates as a feedstock for the chemical industry; be it for bulk, commodity, intermediate, fine or high-value-added speciality chemicals; is modest when considering their ready availability at low cost and their huge as yet unexploited potential. Seven examples realized presently on an industrial scale, i.e. with an annual production of at least 50,000 t/a, are outlined briefly, four involving chemical conversions, three biotransformations.

3.1. LARGE-SCALE PRODUCTS THROUGH CHEMICAL PROCESSING OF CARBOHYDRATE FEEDSTOCKS

Furfural. With an annual production of about 250,000 tons, furfural (2-furaldehyde) appears to be the only unsaturated large-volume organic chemical prepared from carbohydrate sources. The technical process involves exposure of agricultural or forestry wastes to aqueous acid and fairly high temperatures: the β(1→4)-linked D-xyllose and L-arabinose polysaccharides contained in the hemicellulose portion of these waste materials are hydrolysed to the respective pentoses which under the conditions undergo dehydration [McKillip 2000].

Furfural provides a host of industrially important follow-up products (Fig. 3): furfuryl alcohol and its tetrahydro derivative (hydrogenation), furfurylamine (reductive amination), furonic acid (oxidation), furan-acrylic acid (Perkin reaction), or furylidene ketones (aldol condensations). It is also the key chemical for the commercial production of furan (through catalytic decarbonylation) and tetrahydrofuran hydrogenation, thereby providing a biomass-based alternative to its petrochemical production via dehydration of 1,4-butanediol (McKillip 2000).
**Figure 3.** Furanic commodity chemicals derived from pentosans in agricultural wastes (corn cobs, oat hulls, wood chips, etc.).

**D-Sorbitol (≡ D-Glucitol).** Readily produced by hydrogenation of D-glucose (cf. Fig. 4), the main consumer of its sizable annual production (650,000 t/a) is the food industry, primarily as a non-caloric sweetening agent and as a key intermediate for the production of ascorbic acid (vitamin C). However, it has important non-food applications due to its moisture conditioning, softening and plastifying properties. These entail its use in adhesives, paper, printing, textiles, cellulose-based foils, pharmaceutical formulation, and as components in biogradable polyetherpolys in a variety of resins (Vogel 2000).

**D-Gluconic acid.** Its current worldwide production, estimated to be 100,000 t/a, is based on either chemical (e.g. hypochlorite, Pt/O₂), electrochemical or enzymatic
oxidation of D-glucose (Fig. 4). Aside its use in the food processing industry as an acidulant, it has important non-food uses as a metal-etching agent, as a sequestrant in cleaners, and as latent acid catalyst in textile printing [Hustede 2000].

<table>
<thead>
<tr>
<th>Chemical Conversions</th>
<th>Biotransformations</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-Sorbitol 650000 t/a</td>
<td>Pharmaceuticals, Antibiotics, Vitamins</td>
</tr>
<tr>
<td>D-Gluconic Acid 100000 t/a</td>
<td>Ethanol (biofuel) (2004: 25 mll. t)</td>
</tr>
</tbody>
</table>

Glucose (from cornstarch, bagasse, molasses, wood)

\[
x - 0.3-0.7 \\
m = 2-5
\]

Alkyl polyglucosides ("APG's")

**Surfactant**
Cognis (Düsseldorf): 50000 t/a

\[
\text{Polycondensation}
\]

**Polylactic Acid (PLA)**
Cargill (Nebraska): 150000 t/a

*Figure 4*. Large-volume industrial products from glucose-containing raw materials.

**Alkyl-polyglucosides ("APG's")** are produced by several companies – most notably by Cognis with a capacity in the 50 000 t/a range – and are by far the most important non-ionic surfactants. They represent fatty alcohol glucosides with an alcohol chain length
normally between C₈ and C₁₄. Their industrial synthesis either comprises a direct acid-catalyzed Fischer glycosidation of glucose (in the form of a syrup starch hydrolysate) or starch itself (cf. Fig. 4). The alternate process consists of two stages, the first being Fischer glycosidation with n-butanol to butyl glycosides which are subsequently subjected to acid-promoted transacetalization. The resulting product mixtures contain the α-δ-glucosides majorly, as designated in the formula (Fig. 4), and are marketed as such. APG’s are not skin-irritating, have good foaming properties, and are completely biodegradable, hence are widely used in manual dishwashing detergents and in formulations of shampoos, hair conditioners and other personal care products [Hill 1999].

3.2. LARGE-SCALE PRODUCTS THROUGH BIOPROCESSING OF CARBOHYDRATE FEEDSTOCKS

Ethanol ("bioethanol") with a 2004 production of about 24 million tons [WVZ 2004] is the largest volume sugar-based product today. The principal organism for fermentation is Saccharomyces cerevisiae, that can grow on a wide variety carbohydrate feedstocks: sugar crops, and sugar-containing by-products such as sugar cane, sugar beet, sorghum, molasses, and – after hydrolysis to glucose – starchy crops such as corn, potatoes and grains, or cellulosic materials, e.g. wood pulping sludges from pulp and paper mills [Himmel 1997]. The manufacturing costs are said to be roughly the same as those for its production from methylene at a comparable plant size [Goebel 2001].

The large growth in production of industrial-grade fermentation ethanol within recent years is less due to its use as a solvent and starting material for follow-up chemicals such as acetaldehyde, ethyl esters (e.g. EtOAc) and ethers (Et₂O) – these mostly result from ethylene-based processing lines – but from its high potential as a fuel additive, admixible to gasoline to the extent of 5%. However, a hefty government subsidy is required (renouncement of gasoline tax) to remain competitive.

Polyactic Acid (PLA). Substantial amounts of D-glucose – in crude form as obtainable from corn, potatoes or molasses by acid hydrolysis – enter into industrial fermentation processes towards the production of lactic acid, which subsequently is polymerized via its cyclic dimer ("lactide") to polyactic acid (cf. Fig. 4), a high molecular weight polyester [Gruber 2006].

Due to its high strength PLA can be fabricated into fibres, films, and rods that are full biodegradable and compostable. Accordingly, PLA and copolymers of lactic and glycolic acid are of particular significance for food packaging and, in agricultural or gardening applications. Cargill presently produces PLA (tradename “Nature Works”) in its Nebraska plant with an annual capacity of 140,000 t [McCoy 2003].

Pharmaceuticals. Aside the enormous amount of glucose that flows into the fermentative production of amino and hydroxy acids – l-lysine, l-glutamic acid, citric
acid, and D-gluconic acid, of which the major part is for food use — a significant volume is used in fermentation processes furnishing high-value-added products — antibiotics and vitamins, much too complex in their structures as to be generated by chemical synthesis. Representative examples — penicillins and cephalosporins with an estimated world production in the 70,000 t/a range, the aminoglycoside antibiotics of the kanamycin and spectinomycin type, or the recently optimized bioprocesses for bulk-scale production of vitamin C and B6.

4. TOWARDS FURTHER SUGAR-BASED CHEMICALS: POTENTIAL FUTURE DIRECTIONS

Considering the large-scale, low-cost availability of the basic biomass-sugars listed in Table 1, their present non-food utilization by the chemical industry is modest, i.e. the huge feedstock potential lying in carbohydrates in general, and in the low-molecular-weight sugars in particular, is largely untapped. In view of the necessity for the chemical industry to face up to the changeover from fossil raw materials to biofeedstocks — i.e. to carbohydrates primarily as these are better accessible from agricultural crops and waste materials than other natural products — it is imperative that carbohydrates are further exploited, systematically and on a broad scale, towards the production of chemicals and materials which eventually replace those from petrochemical sources — an endeavor that undoubtedly is the major challenge of ‘green’ chemistry in the 21st century.

The process technology for converting petrochemical raw materials into viable organic chemicals and materials is exceedingly well developed and highly efficient. This is not the case for the conversion of carbohydrates into industrially relevant products — except the seven examples mentioned (vide supra) — and, on top of this, the process methodologies required for these transformations are fundamentally different — understandable, as carbohydrates have an inherently more complex structure and composition than fossil raw materials. Today’s refineries and the biorefineries of the future will be very different in the technology used as well as in appearance.

Over the last 15 years various efforts have been made towards the development of efficient, environmentally benign and economically viable process methodologies for industrially relevant products [Lichtenhaler 1991, 1992, Descotes 1993, van Bekkum 1996, Lichtenhaler 1998, 2004, 2006]. Due to the reluctance of the chemical industry to enter R & D work in this field — petro-derived products are still substantially cheaper than their biobased analogs — these efforts were mostly done in academic research groups without coordination by funding institutions. Here, in 2004, a most encouraging conceptual milestone was set by the U.S. Department of Energy by identifying from a list of 300 candidates (1) the top 12 sugar-derived building blocks of Table 2 — bioplatform chemicals so to say, that each has the potential to be converted into a range of value-added chemicals and materials by follow-up transformations [DOE 2004]. Accordingly, these building blocks are most promising candidates for systematically pursuing their full industrial utilization.
Table 2. DOE's top twelve sugar-derived building blocks waiting for industrial exploitation.

<table>
<thead>
<tr>
<th>#</th>
<th>building block</th>
<th>carbon atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>glycerol</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>3-hydroxypropionic acid (3-HPA)</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>succinic acid</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>fumaric acid</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>L-malic acid</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>3-hydroxybutyrolactone</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>L-aspartic acid</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>L-glutamic acid</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>levulinic acid</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>itaconic acid</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>xylitol</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>L-arabinitol</td>
<td>5</td>
</tr>
<tr>
<td>No.</td>
<td>Chemical Name</td>
<td>Molecular Structure</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>10</td>
<td>d-sorbitol</td>
<td><img src="image" alt="d-sorbitol" /></td>
</tr>
<tr>
<td>11</td>
<td>glucaric acid</td>
<td><img src="image" alt="glucaric acid" /></td>
</tr>
<tr>
<td>12</td>
<td>furan-2,5-dicarboxylic acid (FDA)</td>
<td><img src="image" alt="furan-2,5-dicarboxylic acid" /></td>
</tr>
</tbody>
</table>

Each of these bioplatform chemicals, as well as a few others which the author considers to belong into the same category, are being commented up on in the sequel with respect to their present state of industrial realization.

4.1. GLYCEROL

Worldwide production is estimated to be in the range of 750,000 t/a, almost entirely made from natural triglycerides, the sizable amounts resulting from the increasing biodiesel production lowering costs substantially. The technology for generating a variety of industrially important follow-up products is not well developed yet, e.g. 1,2-propanediol (propylene glycol) and 1,3-propanediol – the diol component of the high-performance polyester fiber Sorona® [Dupont 2006] or Corterra® [Shell 2006] presently produced from petrochemical raw materials – could be made from glycerol. Presently, there are substantial research efforts towards elaboration of economically sound bioprocesses for the (formal) dehydroxylations at C-1 to the 1,2-diol [Nishino 2003] as well as C-2 to its 1,3-analog [Zeng 2002, Zhu 2002].
4.2. 3-HYDROXYPROPIONIC ACID (3-HPA)

Like the structurally isomeric lactic acid, it constitutes a three-carbon building block with the potential of becoming a key intermediate for a variety of high-volume chemicals – malonic and acrylic acids, methacrylate, acrylonitrile etc. [DOE 2004]. Cargill is developing a low-cost fermentation route by metabolic engineering of the microbial biocatalyst that produces 3-HPA under anaerobic conditions [Cameron 2003], yet it will take another one to two years for the process to reach commercial viability [Tullo 2005].

4.3. FUMARIC, SUCCINIC AND MALIC ACID

Fumaric acid, a metabolite of many fungi, lichens, mosses and some plants, which is mainly used as the diacid component in alkyd resins [Lohbeck 2000] is produced commercially to some extent by fermentation of glucose with Rhizopus arrhizus [Carta 1999], yet productivity improvements seem essential for the product to be an option for replacing its petrochemical production by catalytic isomerization of maleic acid.

Most of the maleic acid produced, approximately 10 000 t/a, is racemic, because it is derived from petrochemically produced fumaric acid. The L-form can also be produced from fumaric acid by hydration with immobilized cells of Brevibacterium or Corynebacterium species.
Succinic acid is used to produce food and pharmaceutical products, surfactants and detergents, biodegradable solvents and plastics, and ingredients to stimulate animal and plant growth. Although it is a common metabolite formed by plants, animals, and microorganisms, its current commercial production of 15,000 tons per year is from petroleum, i.e. by hydrogenation of malic acid. The major technical hurdles for succinic acid as green, renewable bulk scale commodity chemical – 1,4-butanediol, THF, γ-butyrolactone, or pyrrolidones are industrially relevant products – entail the development of very-low-cost fermentation routes from sugar feedstocks. Currently available anaerobic fermentations of glucose include use of an organism genetically cloned from *Aspergillus succiniproducens*, an engineered *E. coli* strain developed by DOE laboratories [DOE 2004], and several others [Vemuri 2002]. The processes are currently under active development. Production costs must be at or below $0.25 lb⁻¹ to match petrochemical production [DOE 2004].

![Diagram of metabolic pathway](image)

*Figure 5.* Glycolytic pathway leading to the L-malic, fumaric and succinic acids.

4.4. **3-HYDROXYBUTYROLACTONE**

Presently a specialty chemical for fairly high value pharmaceuticals, its generation from starch by oxidative (H₂O₂) degradation is regarded as “messy”, because it involves multiple steps and results in a variety of side-products. Thus, this process must be improved, or alternatives found to fully utilize the potential of this four-carbon building block for the production of a variety of industrially important tetrahydrofuranoid derivatives. One such alternative for its generation would be reduction and cyclization of microbiologically produced L-malic acid.
4.5 ASPARTIC AND GLUTAMIC ACID

It is somewhat surprising that the two naturally occurring amino acids, glutamic acid – a 1.5 mill. t/a commodity chemical used mainly as a flavor enhancer in food – and aspartic acid, industrially exploited only for the sweetener aspartame, are considered by the DOE expert panel [DOE 2004] to belong to the top 12 sugar-based building block chemicals. Although each may be transformed into a family of useful four- and five-carbon building block chemicals – pyrrolidines, pyrrolidones, lactones, diols, aminodiols etc. – the major technical hurdles to be overcome appear to be the development of efficient fermentation routes or substantial improvements to the current technologies in order to significantly reduce production economics.

4.6. LEVULINIC ACID and formic acid are products of the acidic and thermal decomposition of lignocellulosic material, their multi-step formation from the hexoses contained therein proceeding through 2-hydroxymethylfurfural (HMF) as the key intermediate; the hemicellulose part, mostly xylans, furnishes furfural [Klingler 2000]. A commercially viable fractionation technology for the specific, high-yield acquisition of levulinic acid has been developed (“The Biofine Process”) [Fitzpatrick 1999, Hayes 2006]. The first pilot plant with a capacity of 3000 t/a, built by Le Calorie in Caserta, Italy, is expected to go into full production shortly [Ritter 2006].
Levulinic acid is the starting material for a large number of higher-value products, because it can be converted by established procedures into products such as acrylic and succinic acids, pyrrolidines, and diphenolic acid, the latter having the potential of replacing bisphenol A in the manufacture of polycarbonate resins. Thus, the large-scale accessibility of levulinic acid through the “Biofine Process” makes it a viable biorefinery platform chemical.

4.7. ITACONIC ACID

Structurally an α-substituted methacrylic acid (cf. Fig. 4), itaconic acid is a C₅ building block with significant market opportunities. It is currently produced by fungal fermentation at approximately 10,000 t/a¹ and mainly used as a specialty co-monomer in acrylic or methacrylic resins, e.g., incorporation of small amounts into polyacrylonitrile significantly improves the dyeability of the polymer. To become a commodity chemical, productivity improvements with the currently used fungi Aspergillus terreus and Aspergillus itaconicus are required, and progress seems to be encouraging [Reddy 2002]. To be competitive to analogous commodities, the crucial production price of about 0.25 $/lb¹ poses to be reached [DOE 2004] – a significant technical challenge still to be solved.

4.8 XYLITOL AND L-ARABINITOL

Five-carbon sugars such as D-xylose and L-arabinose, abundantly occurring in (1→4)-linked polysaccharide form in hemicelluloses, are readily obtainable by hydrolysis of various woody waste materials, yet are usually further processed to furfural (cf. above). The conversion of the monomeric pentoses to their respective pentitols by reduction — e.g., xylitol, presently used as a non-caloric sweetener — or their C-1-carboxylic and C-1,C-5-dicarboxylic acids by oxidation (e.g., D-xylonic and xylaric acid, resp.) appear within technical reach for bulk scale production (Fig. 6), although the efficiency for oxidation to the dicarboxylic acids, which have significance for the preparation of polyesters and polyamides, will have to be improved. Another industrial outlet could become the production of glycol and 1,2-propanediol through hydrogenolysis of the either pentose or pentitol.
Figure 6. Five-carbon building blocks from hemicellulosic xylans (other than furfural).

4.9. D-SORBITOL

Due to its highly efficient production by hydrogenation of D-glucose and its extensive use in the food, paper and textile industry (cf. above), D-sorbitol already is a bulk scale product (ca. 900 000 t/a presently) [Vogel 2000], yet there are some indications that its accessibility (and price) may be improvable by exposing cellulose directly to hydrogenation catalysts supported on zeolites (Fukuoka 2006). Thus, it has significant potential as an inexpensive feedstock for commodity chemicals, most notably for the production of glycol and propylene glycol via hydrogenolysis, as well as 1,4-sorbitan and isosorbide via dehydration – furanoid di- and tetra-alcohols that have already found use in the form of mono-fatty acid esters (R = C_16-C_18-acyl) as surfactants. All of these building blocks are of course ideal alcohol components for the generation of polyesters.
4.10. SUGAR-DERIVED DICARBOXYLIC ACIDS

Although malic, tartaric, aspartic and glutamic acid are sugar-derived dicarboxylic acids with industrial significance as building block chemicals, major importance are to have those sugar dicarboxylates that fully utilize the entire carbon chain of the key sugars of biomass, rather than parts of it. Thus, not only \textit{D-glucaric} and \textit{furan-2,5-dicarboxylic acid}, selected by the DOE expert panel to belong to the top 12 building blocks worthy of further industrial exploitation [DOE 2004] but a variety of others as well, such as the \textit{xylaric} and \textit{galactaric acids} (cf. Fig. 8), as well as those derived from bulk scale available disaccharides, \textit{sucrose-6,6-dicarboxylic acid} most notably.
D-Glucaric acid is a direct nitric acid oxidation product of glucose or starch [Mehlertter 1963], usually isolated as its 1,4-lactone, galactaric and xylaric acid, accessible from lactose [Lewis 1963] and from d-xylose or hemicellulosic xylans. The technical barriers to their large-scale production are mainly development of efficient and selective oxidation technology for these sugars to eliminate the need for nitric acid.
as oxidant. Investment in Pt-catalyzed oxidation with oxygen seems to be a promising approach.

Sucrose being cheaper than its component sugars D-glucose and D-fructose, and available in exceptional purity and unprecedented quantities (cf. Table 1) and carboxylic acids resulting from selective oxidation of its primary hydroxyl groups are apt to be of even higher industrial relevance. Due to the persistence of an intersaccharidic water-bridge of the 2'-HO - - HO-1' type in aqueous solution [Inmem 1995], oxidation of sucrose with air in the presence of 0.5 % Pt/C at 35 °C gives a 9:9:1 ratio of the 6', 6'- and 1'-saccharonic acids [Kunz 1994]. On further oxidation, particularly when using large amounts of the Pt catalyst and higher temperatures (80-100 °C), the preferred formation of sucrose-6',6'-dicarboxylic acid has been observed [Edye 1991], yet a preparatively useful procedure for its acquisition was developed only recently [Kunz 1996] through combining Pt/air-oxidation with continuous electrodialytic removal of the diacid, thereby protecting it from further oxidation.

![Figure 9. Catalytic oxidation of sucrose.](image)

Similar industrial potential is to be attributed to the isomaltulose-derived glucuronyloxymethyl furoic acid readily obtained from sucrose-derived, large scale-produced (80 000 t/a) isomaltulose through acid treatment [Lichtenthaler 1993] and subsequent catalytic oxidation [Cuny 2006]. It is a unique building block as it combines a distinctly hydrophilic with a hydrophobic part, which, when 'extended' by
esterification with fatty acids provides products with liquid crystal properties (Hansmann 1992).

The high industrial potential of furan-2,5-dicarboxylic acid, accessible from fructose or fructosans (inulin) via 5-hydroxymethylfurfural (‘HMF’) [Kuster 1990, Bicker 2003], is particularly obvious as it could replace petroleum-derived diacids such as adipic or terephthalic acid in the production of polyesters and polyamides. Indeed, an impressive series of furan polyesters and polyamides has been prepared [Gandini 1997, Moreau 2004], in which furandicarboxylic acid replaces terephthalic and isophthalic acids. None, however, has proved economically competitive to the products currently on the market, the major impediment not being somewhat different properties but the technical hurdles still to be solved to efficiently and economically produce HMF. It’s generation from fructose or inulin hydrolysates are simply too expensive as starting materials for its production, and yields based on glucose-based waste materials are as yet not exceeding 40 %. This situation entails that HMF currently appears in chemical catalogs with prices of 37 € [TCI 2006] to 44 € [Fluka 2007] per gram (1).

To become a biorefinery platform chemical the technical hurdles for generating HMF with high efficiency from agricultural or forestry waste materials will have to be solved – a formidable task. Only then, the follow-up products, e.g. furan-2,5-dicarboxylic acid will become an attractive option for replacing petrochemical analogs, but a variety of other platform chemicals as well, since large-scale-adaptable procedures for their acquisition from HMF are well worked out: the 5-hydroxymethylfuroic acid, the 1,6-diamine, and the respective 1,6-diol (framed formulae in Fig. 10); they are most versatile intermediate chemicals of high industrial potential, because they are six-carbon monomers that could replace adipic acid, or alkyl diols, or hexamethylenediamine in the production of polyamides and polyesters.
5. CONCLUSION

The non-food utilization of inexpensive, bulk scale-accessible low-molecular-weight carbohydrates — sucrose, glucose, xylose and fructose being the most readily accessible — is at a rather modest level in terms of large-scale manufactured commodities currently on the market. They amount to about 5% only of the entire chemicals and materials presently produced. As the chemical industry though is forced to shift to a more biobased production system — for compelling environmental reasons as well as the depletion of fossil resources — the utilization of carbohydrates as the raw materials are to increase substantially (dotted curves in Fig. 1). The conceptual framework along which this is to occur is clear: systematic further development of practical, large-scale adaptable transformations of sugars to building blocks that have
the potential to replace those currently made from petrochemical raw materials. In this
endeavour, the selection of the 12 top sugar-derived building block chemicals by the
DOE (cf. Table 2) is an important milestone in focussing R & D efforts, yet a large
number of other “reaction channels” from sugars to industrially relevant, economically
viable products are waiting for their exploitation – a task that can successfully be
achieved only if the present chemical methodology is utilized to its fullest and the
increasingly emerging biotechnological procedures as well. All of this, unambiguously,
points towards broad-scale, practicality-oriented basic and applied research to be
performed not only in academic institutions, but also in industrial laboratories, most
effectively, of course, if both cooperate closely. In short, the challenges for the 21st
century, at least in outline form, are clear. The capacity to develop vibrant and inciteful
collaborations between academic and industrial institutions – hopefully generously
supported by national and/or international funding institutions (the next EU framework
program 7) – are likely to emerge as the new frontier towards the industrial utilization
of carbohydrates which Nature offers us on an annual basis. Economically sound
biobased alternatives to petrochemicals – highly promising examples are contained in
this account – will then become available as a matter of course.

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