Chemicals from renewable biomass
A renaissance in carbohydrate chemistry

Sheldon, Roger A.

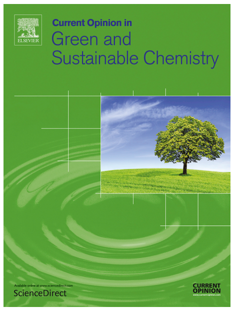
DOI
10.1016/j.cogsc.2018.08.003

Publication date
2018

Document Version
Accepted author manuscript

Published in
Current Opinion in Green and Sustainable Chemistry

Citation (APA)
Sheldon, R. A. (2018). Chemicals from renewable biomass: A renaissance in carbohydrate chemistry. *Current Opinion in Green and Sustainable Chemistry*, *14*, 89-95. https://doi.org/10.1016/j.cogsc.2018.08.003



Chemicals from Renewable Biomass: a Renaissance in Carbohydrate Chemistry

Roger A. Sheldon

PII: S2452-2236(18)30072-5
DOI: 10.1016/j.cogsc.2018.08.003
Reference: COGSC 202

To appear in: *Current Opinion in Green and Sustainable Chemistry*

Received Date: 4 July 2018
Revised Date: 31 July 2018
Accepted Date: 6 August 2018

Please cite this article as: R.A. Sheldon, Chemicals from Renewable Biomass: a Renaissance in Carbohydrate Chemistry, *Current Opinion in Green and Sustainable Chemistry* (2018), doi: 10.1016/j.cogsc.2018.08.003.

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.

Addresses

1. Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Braamfontein, Johannesburg 2050, South Africa.

2. Department of Biotechnology, Delft University of Technology, Delft, Netherlands

E-mail: roger.sheldon@wits.ac.za

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.

References

Papers of particular interest published within the period of review have been highlighted as:

***** of special interest
** of outstanding interest

1. Deneyer A, Ennaert T, Sels, BF: Straightforward sustainability assessment of sugar-derived molecules from first-
* generation biomass. *Curr. Opin. Green Sust. Chem*. 2018, 10:11-20.

This report selects four criteria, taking into account the entire valorization chain, to evaluate carbohydrate-derived molecules

2. Sheldon RA: **The Road to Biorenewables: Carbohydrates to Commodity Chemicals**. *ACS Sust Chem Eng* 2018, **118 (2)**, 747–800. .
3. Zhang Z, Huber GW: **Catalytic oxidation of carbohydrates into organic acids and furan chemicals.** *Chem. Soc. Rev*. 2018, **47**, 1351-1387.
4. Ruppert AM, Weinberg, KM, Palkovits, R: **Hydrogenolysis goes Bio : From Carbohydrates and Sugar Alcohols to Platform Chemicals**. *Angew Chem Int Ed* 2012, ***51***, 2564-2601.
5. Chatterjee C, Pong F, Sen A: **Chemical conversion pathways for carbohydrates**. *Green Chem* 2015, **17**, 40-71.
6. * Nielsen J, Keasling J: **Engineering Cellular Metabolism**. *Cell*, 2016, **164**, 1185-1197.

Reviews the current status and challenges of metabolic engineering.

7. Jullesson D, David F, Pfleger B, Nielsen J: **Impact of synthetic biology and metabolic engineering on industrial production of fine chemicals**. *Biotechnol. Advan*. 2015, **33**, 1395-1402.
8. Straathof AJJ: **Transformation of Biomass into Commodity Chemicals Using Enzymes or Cells**. *Chem Rev* 2014, **114**, 1871-1908.
9. M. J. Burk and S, Van Dien, **Biotechnology for Chemical Production: Challenges and Opportunities**. *Trends Biotechnol*. 2016, **34**, 187-190.

10. S. Van Dien, **From the first drop to the first truckload: commercialization of microbial processes for**
** **renewable chemicals** *Curr. Opin. Biotechnol*. 2013, **24**, 1061-1068.

Clearly explains what is necessary to achieve commercial viability with fermentations.

11. Statista: https://www.statista.com/statistics/274142/global-ethanol-production-since-2000/ Last visited July 2018

12. Horváth, I. T.: Cséfalvay, E.; Mika, L. T.; Debreczeni, M. Sustainability Metrics for Biomass-Based Carbon
* Chemicals. *ACS Sustainable Chem. Eng*. 2017, **5**, 2734-2740.

A novel approach to developing sustainability metrics for commodity chemicals from biomass.

13. Jang MO, Choi G: **Techno-economic analysis of butanol production from lignocellulosic biomass by concentrated acid pretreatment and hydrolysis plus continuous fermentation.** *Biochem. Eng. J*. 2018, **134**, 30-43.

14. Jung HM, Lee JY, Lee JH, Oh MK: **Improved production of isobutanol in pervaporation-coupled bioreactor using sugarcane bagasse hydrolysate in engineered Enterobacter aerogenes**. *Bioresour Technol.* 2018, **259**:373-380.

15. van Leeuwen BNM, van der Wulp AM, Duijnstee I, van Maris, AJA, Straathof AJJ**: Fermentative production of isobutene**. *Appl. Microbiol. Biotechnol*. 2012, **93**, 1377-1387.

16. Yang, J.; Nie, Q.; Liu, H.; Xian, M.; Liu, H. **A novel MVA-mediated pathway for isoprene production in engineered *E. coli*.** *BMC Biotechnology,* 2016, 16**:5**.

17. Kim JH, Wang C, Jang HJ, Cha MS, Park JE, Jo SY, Choi ES, Kim SW: **Isoprene production by *Escherichia coli* through the exogenous mevalonate pathway with reduced formation of fermentation byproducts**. *Microb Cell Fact*. 2016, *15*: 214.

18. Tippmann S, Scalcinati G, Siewers V, Nielsen J: **Production of farnesene and santalene by Saccharomyces cerevisiae using fed-batch cultivations with RQ-controlled feed**. *Biotechnol Bioeng.* 2016, **113(1)**:72-81.

19. Beller HR, Rodrigues AV, Zargar K, Wu YW, Saini AK, Saville RM, Pereira JH, Adams PD, Tringe SG, Petzold CJ,
** Keasling JK: **Discovery of enzymes for toluene synthesis from anoxic microbial communities**. *Nature Chem.Biol.* 2018,**14(5)**: 451-457.

A new milestone in metabolic engineering, enabling fermentative production of aromatic hydrocarbons.

20. Jiang Y, Liu W, Zou H, Cheng T, Tian N, Xian M: **Microbial production of short chain diols**. *Microbial Cell Factories* 2014, **13**:165.

21. Nakamura CE, Whited GM: **Metabolic engineering for the microbial production of 1,3-propane diol**. *Curr Opin*
* *Biotechnol* **2003**, **14**, 454-459.

The watershed example of modern biotechnology for biobased production of a commodity chemical.

22. Lee JH, Lama S, Kim JR, Park SH: **Production of 1,3-Propanediol from Glucose by Recombinant *Escherichia coli* BL21(DE3*).*** *Biotechnol. Bioprocess Eng.* 2018, 23, 250-258.

23. Burgard A, Burk MJ, Osterhout R, Van Dien S, Yim H: **Development of a commercial scale process for**
** **production of 1,4-butanediol from sugar**. *Curr. Opin. Biotechnol*, 2016, **42**, 118-127.

A *tour de force* example of metabolic engineering of a heterologous pathway for 1,4-butane diol production.

24. Barton NR, Burgard AP, Burk MJ, Crater JS, Osterhout RE, et al, **An integrated biotechnology platform for developing sustainable chemical processes** . *J. Ind. Microbiol. Biotechnol.* 2015, **42**, 349-360.

25. Thongchul N: **Production of Lactic Acid and Polylactic Acid for Industrial Applications**, Chapter 16 in Yang ST, El-Enshasy HA, Thongchul N (Eds.): Bioprocessing Technologies: Biorefinery for Sustainable Production of Fuels, Chemicals and Polymers, Wiley, Hoboken, **2013**. pp. 293-316.

26. Canete-Rodriguez AM, Santos-Duenas IM, Jimenez-Hornero JE, Ehrenreich A, Liebl W, Garcia-Garcia I: **Gluconic acid: Properties, production methods and applications—An excellent opportunity for agro-**

industrial by-products and waste bio-valorization . *Proc. Biochem.* 2016**, 51,** 1891-1903.

27. Krull S, Hevekerl A, Kuenz A, Prüβe U: **Process development of itaconic acid production by a natural wild type strain of *Aspergillus terreus* to reach industrially relevant final titers**. *Appl. Microbiol. Biotechnol*. 2017, **101**, 4063-4072.

28. Robert T, Friebel S: **Itaconic acid – a versatile building block for renewable polyesters with enhanced functionality**. *Green Chem***.**, 2016**, 18,** 2922-2934.

29. Le Nôtre J, Witte-van Dijk SC, van Haveren J, Scott EL, Sanders JP: **Synthesis of Bio-Based Methacrylic Acid by Decarboxylation of Itaconic Acid and Citric Acid Catalyzed by Solid Transition-Metal Catalysts**. *ChemSusChem*. 2014, **7**, 2712-2720.

30. Ferone M, Raganati F, Olivieri G, Salatino P, Marzocchella A: Biosuccinic Acid from Lignocellulosic-Based Hexoses and Pentoses by Actinobacillus succinogenes: Characterization of the Conversion Process. *Appl Biochem Biotechnol.* 2017, **183(4):**1465-1477.

31. Dishisha T, Pyo SH, Hatti-Kaul R: **Bio-based 3-hydroxypropionic- and acrylic acid production from biodiesel glycerol via integrated microbial and chemical catalysis**. *Microb Cell Fact.* 2015,14:200.

32. Kruyer NS, Peralta-Yahya P: **Metabolic engineering strategies to bio-adipic acid production.** *Curr Opin Biotechnol.* 2017, **45**:136-143.

33. http://www.rennovia.com/wp-content/uploads/2017/02/Johnson-Matthey-and-Rennovia-Announce-License-Agreement-with-ADM-for-Glucaric-Acid-Production-Technology-Press-Release-2-21-2017-1.pdf Last visited June 2018.

34. Zada B, Chen M, Chen C, Yan L, Xu Q, Li W, Guo Q, Fu Y: **Recent advances in catalytic production of sugar alcohols and their applications**. *Sci. China Chem*. 2017, **60**, 853-869.

35. Zheng M, Pang J, Sun R, Wang A, Zhang T: **Selectivity Control for Cellulose to Diols: Dancing on Eggs**. *ACS Catal*. 2017, **7**, 1939-1954.

*

Provides a clear mechanistic analysis of the pathways to the different diols.

36. van Putten RJ, van der Waal JC, de Jong E, Rasrendra CB, Heeres HJ, de Vries JG: **Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources**. *Chem. Rev*. 2013, **113**, 1499–1597.

37. Kucherov FA, Romashov LV, Galkin KI, Ananikov VP: **Chemical Transformations of Biomass-Derived C6-Furanic Platform Chemicals for Sustainable Energy Research, Materials Science and Synthetic Building Blocks***. ACS Sust. Chem. Eng*. 2018 DOI: 10.1021/acssuschemeng8b00971.

38. Wang J, Xi J, Xia Q, Liu X, Wang Y: **Recent advances in heterogeneous catalytic conversion of glucose to 5-hydroxymethylfurfural via green routes**. *Sci. China Chem*. 2017, **60**, 870-886.

*

A good overview of the challenges in converting glucose to HMF.

39. Li M, Li W, Lu Y, Jameel H, Chang HM, Ma L: **High conversion of glucose to 5-hydroxymethylfurfural using hydrochloric acid as a catalyst and sodium chloride as a promoter in a water / γ- valerolactone system**. *RSC Adv.*, 2017, **7**, 14330-14336.

40. Alipour S, Omidvarborna, H, Kim DS: **A review on synthesis of alkoxymethyl furfural, a biofuel candidate**. *Renew. Sust. Energy Rev.* 2017, **71**, 908-926.

41. https://www.synvina.com/ Last visited July 2018.

42. http://www.sustainablebrands.com/press/dupont_corbion_synvina_pilot_furan-based_polymers_made_sugar_must_confront_pet%E2%80%99s_dominance Last visited July 2018.

43 Eerhart A JJE, Faaij APC, Patel PK: **Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance**. *Energy. Environ. Sci*. 2012, **5**, 6407-6422.

---

44. *https://www.avantium.com/yxy/products-applications/* Last visited July 2018.

45. Zhang Z, Zhou P: **Catalytic Aerobic Oxidation of 5-Hydroxymethylfurfural (HMF) into 2,5-Furandicarboxylic Acid and Its Derivatives**. In: Fang Z., Smith, Jr. R., Qi, X. (eds) Production of Platform Chemicals from Sustainable Resources. Biofuels and Biorefineries. Springer, Singapore, 2017, pp. 171-206.

46. Zhang Z, Deng K: **Recent Advances in the Catalytic Synthesis of 2,5-Furandicarboxylic acid and its Derivatives**. *ACS Catal*. 2015, **5**, 6529-6544.

47. Motagamwala AH, Won W, Sener C, Alonso DM, Marvelias, CT, Dumesic JA: **Toward biomass-derived renewable plastics: Production of 2,5-furandicarboxylic acid from fructose**. *Sci Adv*. 2018, **4: eaap 9722**, 1-8.

48. Liu B, Ren Y, Zhang Z: **Aerobic oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid in water under mild conditions**. *Green Chem*. 2015, **17**, 1610-1617.

49. Zheng L, Zhao J, Du Z, Zong B, Liu H: **Efficient aerobic oxidation of 5-hydroxymethylfufural to 2,5-furandicarboxylic acid on Ru/C catalysts**. *Chem. Sci. China* 2017, 60, 950-957.

50. Dijkman WP, Binda C, Fraaije MW, Mattevi A: **Structure-Based Enzyme Tailoring of 5-Hydroxymethylfurfural**
** **Oxidase**. *ACS Catalysis*, 2015, **5**, 1833-1839.
Remarkably, 5-hydroxymethyl furfural oxidase (HMFO) catalyzes all three steps in the oxidation of HMF to FDCA.

51. McKenna SM, LeimKühler S, Hetere S, Turner NJ, Carnell AJ: **Enzyme cascade reactions: synthesis of furandicarboxylic acid (FDCA) and carboxylic acids using oxidases in tandem**. *Green Chem*. 2015, **17**, 3271-3275.

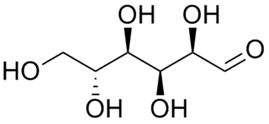
52. Wiercxk N, Elink Schuurman TD, Blank LM, Ruijssenaars HJ: **Whole-Cell Biocatalytic Production of 2,5-Furandicarboxylic Acid**, in Kamm B: Editor, *Microorganisms in Biorefineries*, Springer, Berlin, 2014, 207-223.

53. Miller DJ, Peereboom L, Wegener E, Gattinger M: **Formation of 2,5-furandicarboxylic acid from aldaric acids**. US 9701652 B1 2017 to Board of Trustees of Michigan State University.

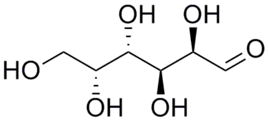
54. van Es DS, van Haveren J, Raaijmakers HWC, van der Klis F, van Engelen GPFM: **Catalytic oxidation of uronic acids to aldaric acids**. WO 2013/151428 A1 to Stichting Dienst Landbouwkundig Onderzoek.

55. Leijdeckers AGM, Bink JPM, Geutjes S, Schols HA, Gruppen H: **Enzymatic saccharification of sugar beet pulp for the production of galacturonic acid and arabinose; a study on the impact of the formation of recalcitrant oligosaccharides**. *Bioresour. Technol*. 2013, **128**, 518-525.

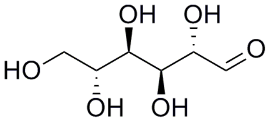
56. Van der Klis F, van Haveren J, van Es DS, Bitter JH: **Synthesis of Furandicarboxylic Acid Esters from Nonfood**
* **Feedstocks without Concomitant Levulinic Acid Formation**. *ChemSusChem*, 2017, **10**, 1460-1468.
Interesting alternative synthesis of FDCA from sugar beet pulp.



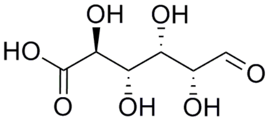
D-glucose



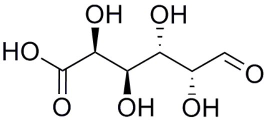
D-galactose



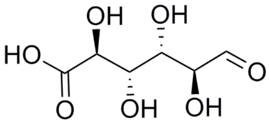
D mannose



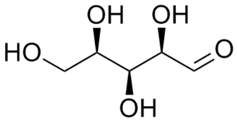
D-glucuronic acid



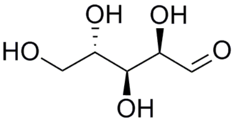
D-galacturonic acid



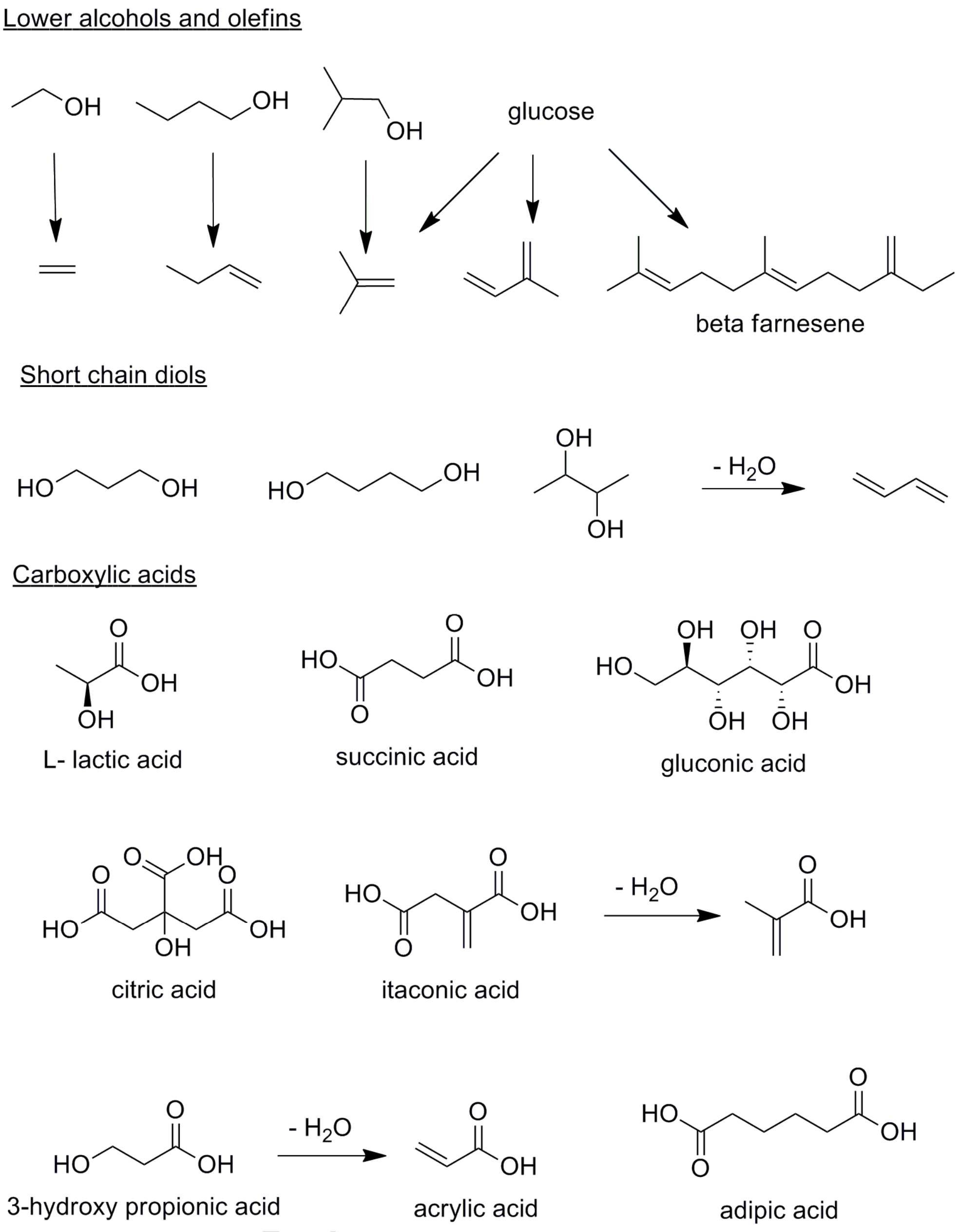
D mannuronic acid

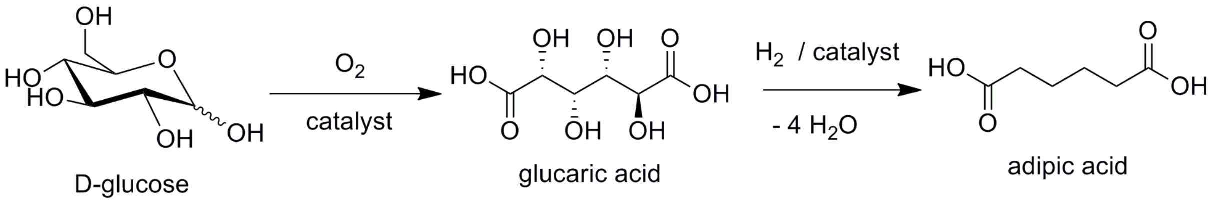


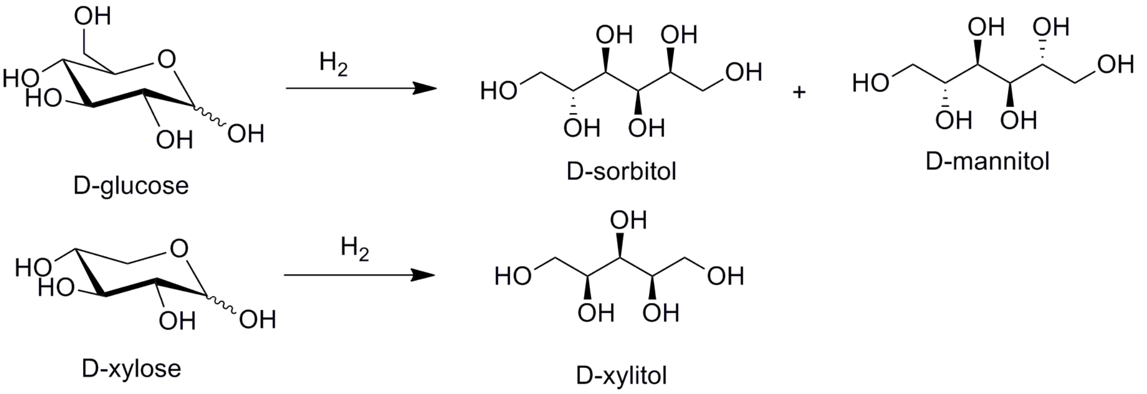
D-xylose

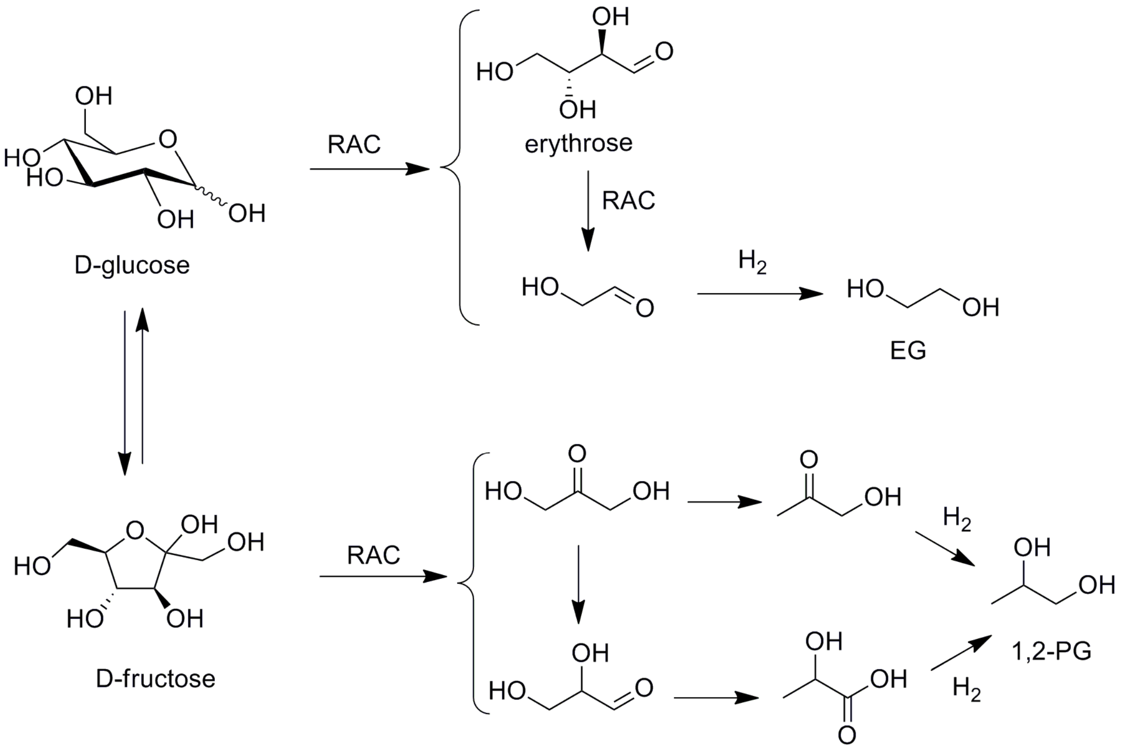


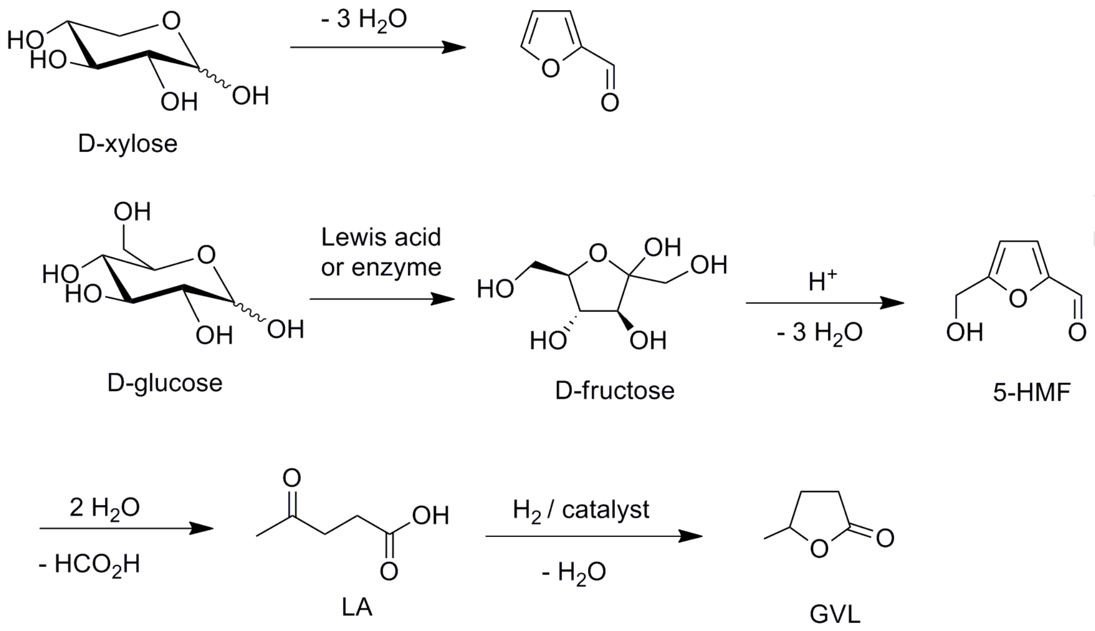
L arabinose

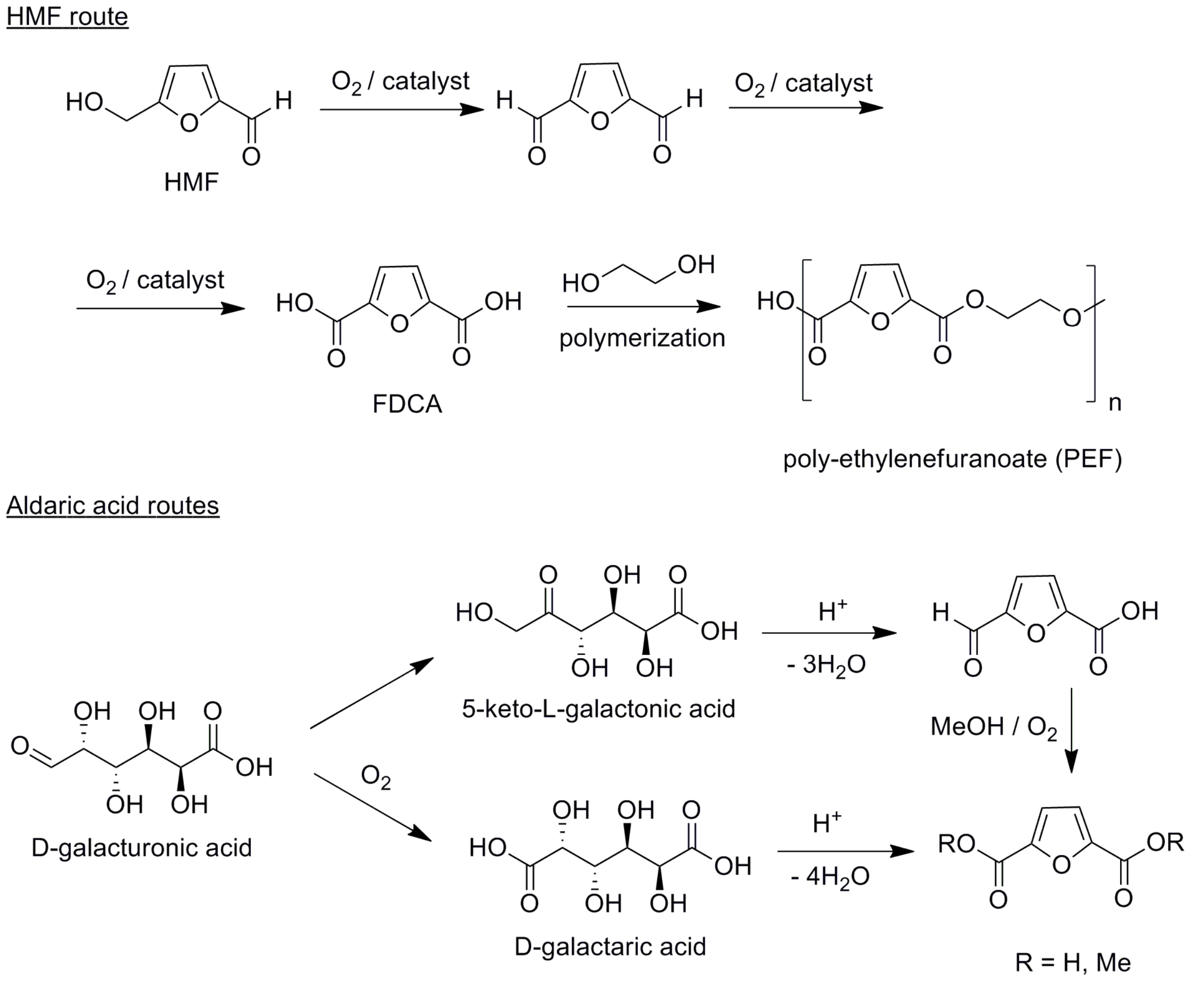

Lower alcohols and olefins
OH
OH
OH
glucose
beta farnesene
Short chain diols
HO
OH
HO
OH
OH
OH
- H_2O
Carboxylic acids
L- lactic acid
succinic acid
gluconic acid
citric acid
itaconic acid
- H_2O
3-hydroxy propionic acid
- H_2O
acrylic acid
adipic acid


OH
O
HO
HO
OH
OH
D-glucose
O_2
catalyst
OH
OH
O
HO
OH
O
OH
OH
glucaric acid
H_2 / catalyst
- 4 H_2O
HO
O
O
OH
adipic acid


D-glucose
H2
D-sorbitol
+
D-mannitol
D-xylose
H2
D-xylitol


D-glucose
RAC
erythrose
RAC
H2
EG
D-fructose
RAC
H2
H2
1,2-PG


D-xylose
- 3 H_2O
D-glucose
Lewis acid or enzyme
D-fructose
H^+
- 3 H_2O
5-HMF
2 H_2O
- HCO_2H
LA
H_2 / catalyst
- H_2O
GVL


HMF route
HO
H
O
HMF
O2 / catalyst
H
O
O
H
O
O2 / catalyst
O2 / catalyst
HO
O
OH
O
O
FDCA
HO
OH
polymerization
HO
O
O
O
O
O
n
poly-ethylenefuranoate (PEF)
Aldaric acid routes
OH
OH
O
O
OH
OH
OH
D-galacturonic acid
O
OH
O
HO
OH
OH
OH
5-keto-L-galactonic acid
H+
- 3H2O
H
O
OH
O
O
MeOH / O2
O2
OH
OH
O
HO
OH
O
OH
OH
D-galactaric acid
H+
- 4H2O
RO
O
OR
O
O
R = H, Me