



The role of water in catalytic biomass-based technologies to produce chemicals and fuels

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ABSTRACT

Water can have many different roles in catalytic biomass-based technologies to produce chemicals and fuels. Since water is one of the two basic chemicals of nature used during photosynthesis, biomass contains different amount of water, which can be advantageously utilized during the conversion schemes. Water could be the solvent of the reactions or just either the eliminated product or the reactant resulting in hydration and hydrolysis. Since some of these roles are intrinsically part of the natural system, their change could be very difficult or not even possible. Therefore, the designer of the chemistry or the process must understand the possible roles of water at both the molecular and the macroscopic levels.

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1. Introduction

Water is one of the most abundant molecules on Earth which has its own global cycle [1]. It plays many important roles by providing a very stable and mostly neutral medium for life [2], serving as solvents for many different reactions, and participating in a large number of chemical transformations [3,4]. The water cycle involves a continuous global distillation process resulting in two distinct aqueous environments having higher and lower level of dissolved salts – 96.5% salted water and 2.6% fresh water. While the salted water in the oceans and seas contains dissolved sodium chloride and some other salts that make it useless for human consumption, fresh water in our rivers and lakes generally contains much less salts and other solutes. Consequently, evolution has adjusted the chemistry of the living habitats of the two different aqueous environments [5]. Unfortunately, human activities have increased the levels of dissolved man-made contaminants, including inorganic and organic chemicals and materials, which could have very negative health and environment effects. The societal acceptance of the potential negative impacts of “dirty water” [6] and the recognition of the important role of pollution prevention or “green chemistry” [7], we are discharging less and less contaminated water to the environment because of the increased use of cleaner technologies

as well as closed waste water systems combined with state-of-the-art waste water treatment technologies.

Although the complete depletion of coal, crude oil, and natural gas will probably take several centuries if not millennia, we should produce more and more carbon-based chemicals from biomass to slow the depletion of the fossil resources and use carbon neutral consumer products [8]. Interestingly, the largest component of biomass is water, which could be as little as few percent in an old tree, but as high as 80% of corn kernel or living cells [9]. If our drive to use biomass-based technologies for the production of all carbon-based consumer products will be successful, the volume of water from converted biomass could be large enough to consider it for the production of drinking water. Because of the aqueous nature of biomass, most of the molecules involved are highly functional and many have oxygen-containing functional groups. This can be simply demonstrated by carbon, hydrogen, oxygen, and nitrogen content of the dry matter of biomass and younger components of fossil resources (Table 1).

Conventional productions of carbon-based chemicals and fuels are based on the separation of saturated and aromatic hydrocarbon constituents of fossil resources followed by the introduction of oxygen, nitrogen, and sulfur containing functional groups. In contrary, most of the components of biomass are multifunctional and their conversion to chemicals and fuels require selective defunctionalization. One of the key strategies of the development of successful biomass-based chemical and fuel industry is how to match the properties of the components of biomass with proper

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Table 1
Elemental composition of materials on dry weight basis.

	Carbon (wt%)	Hydrogen (wt%)	Oxygen (wt%)	Nitrogen (wt%)	Sulfur (wt%)	Ref.
Miscanthus fresh	47.3–47.6	5.77–5.95	42.1–43.5	0.33–0.45	0.05–0.08	[10,11]
Switchgrass	43.5–47.5	5.75–6.18	37.57–44.82	0.36–0.77	0.04–0.19	[12,13]
Sorghum stalk	40.0–46.1	5.20–5.76	40.63–40.70	0.39–1.40	0.20–0.27	[14,15]
Sugar cane bagasse	48.6	5.87	42.85	0.16	0.04	[12]
Wheat straw	42.9–47.6	5.11–5.8	40.39–42.41	0.43–0.73	0.09–0.29	[16,17]
Straw (average)	45–47	5.8–6.0	40–46	0.4–0.6	0.05–0.2	[18]
Corn stover	42.60	5.06	36.52	0.83	0.09	[18]
Bark	48–52	5.7–6.8	24.3–40.2	0.3–0.8	< 0.05	[18]
Forest residues	48–52	6.0–6.2	40–44	0.3–0.5	< 0.05	[18]
Wood without bark	48–52	6.2–6.4	38–42	0.1–0.5	< 0.05	[18]
Peat	52–56	5.0–6.5	30–40	1–3	0.05–0.3	[18]
Black coal	76–87	3.5–5.0	2.8–11.3	0.8–1.5	0.5–3.1	[18]
Lignite (North-Dakota)	31.80	4.51	26.35	0.59	0.84	[18]
Bituminous coal (Pennsylvania coal)	83–89	4–6	3–8	1.4–1.6	1.4–1.7	[18]
Anthracite (Pennsylvania coal)	91–94	2–4	2–5	0.6–1.2	0.6–1.2	[18]

conversion technologies to produce the products with minimal structural changes and by energy efficient methods. For example, it seems counter intuitive to use vegetable oils for the production of a highly functionalized product and *vice versa* use carbohydrates for the production of alkanes.

2. Discussion

The production of biomass-based chemicals and fuels should consider the relationships of the chemical composition of the feedstocks and the product(s) including the molecular structure of their constituents. Water is an intrinsic part of biomass, which could be as little as few percent in an old tree, but as high as 80% in plants (Table 2) and living cells. Therefore, the overall efficiency of the conversion of biomass is highly dependent on how well can be matched its water content with the conversion technology, as the removal of excess water could be extremely energy demanding. In this chapter, we provide a short summary of the water content of various biomass resources; the pre-treatment processes involving water followed by the review of conversion opportunities using water as a solvent and/or as a reagent.

2.1. Water contents of various biomass resources

In general, grains with moisture contents from 12 to 22 wt% (based on wet weight) are mature enough to be harvested and dry enough for storage. While switch grasses and Miscanthus usually have lower, the stalk of sugarcane and sweet sorghum have significantly higher water content than grains. Stalks have 67–72 wt% water, which is frequently squeezed to form a “raw juice” resulting in an easily accessible sugar rich aqueous raw material.

With the exception of direct energy generation, the utilization of biomass often requires physical and/or chemical pre-treatment in order to modify advantageously the physical and/or chemical structures of the components. The most frequently used process is the hydrolysis, which converts polysaccharides to mono- and disaccharides. For the enzymatic conversion of the latter to ethanol [30,31], butanol and acetone [32], and lactic acid [33], higher moisture content could be an advantage since the enzymatic reactions are performed in aqueous environments.

Biomass wastes are generally classified into three main groups: forestry residues, agricultural residues, and food wastes (Table 3). Forestry residues are commonly divided into primary and secondary residues. Primary residues accruing from cultivation and secondary residues are produced by the wood processing industry. Although forest product industries could generate the same residues and they could have been used as raw materials, they are beyond the scope of this review.

While forestry residues are usually combusted in power generation plants, high water content of the biomass could have negative effects on the overall energy output [34]. Pre-drying of forestry residues can decrease the water content to the typical value of 8–10 wt% leading to better combustion properties. Alternatively, forestry residues with high moisture levels can be burned with coal [35].

Considering other types of utilizations such as extraction of cellulose and its conversion to sugar *via* hydrolysis [30], and anaerobic digestion to biogas [57], the water content is a required component in these technologies.

Agricultural residues are produced and collected at land fields. By far, the largest source of crop residues is the straw and stover from grain crops representing a wide range of moisture content. Those having higher moisture content are suitable for forage or fermentation. While dry biomass, such as straws, can be utilized *via* gasification or combustion to produce energy, wet biomass has been used for chemical transformations or fermentation to produce chemicals. Biomass with even high water and nutrient content is usually used for forage.

Animal excrements, manure and slurry can be considered as a significant part of agricultural residues [53]. Among the various livestock, the largest population include swine, cattle and poultry, which generate an enormous volume of slurry and manure, for example, China's manure production was 1900 million tons in 2010 [58]. The water content of slurry can be as high as 99.5 wt% so it is used for land applications in crop fields. (Table 4) [59]. Due to its nutrient content, solid manure can be dispersed on crop fields as fertilizer, however, its volume is influenced by physical, chemical and biological properties of the soil as well as local environmental standards [60]. Although surplus manure was treated as waste in the 1990s [60], its valorization has become an issue in the last two decades.

Additional treatment and utilization technologies are based on composition analysis (Table 5) including composting [63], anaerobic digestion, and co-composting with municipal wastes [64]. Since dairy cattle manure contains the highest level of lignocellulose, its hydrolysis to monosaccharides [65] is a possible form of utilization.

Food wastes can be produced before and during the preparation of meals as well as discarded in the manufacturing/production, distribution, wholesale/retail and food service sectors including restaurants, schools and hospitals. Food wastes consist of a broad range of chemicals and materials and moisture content could be as high as 70–80%.

While composting has become less important in the last two decades due to the large area requirements and VOC formation, the anaerobic digestion has gained increased attention as a better processing alternative for food waste aiming to produce biogas

Table 2
Moisture contents of biomass resources.

Biomass	Types	Moisture (wt%)	References
Corn	Grain at harvest time	20–22	[19]
	Grain as the market standard	15.5	[20]
	Clean grain stored with aeration	13–15	[21]
	Shelled grain	15.5	[22]
Barley	Clean grain stored with aeration	12–14	[21]
	Mature grain on the plant	30–50	[23]
	Grain at harvest time	12.5–18	[23]
Miscanthus	Sinensis Gracillimus type	12.51	[10]
	Silberfeder type	14.54	[10]
Oats	Clean grain stored with aeration	12–14	[21]
Rye	Clean grain stored with aeration	12–13	[21]
Sorghum	Clean grain stored with aeration	13–13.5	[21]
	Stalk harvested in November in Greece	67.20	[24]
	Stalk of sweet sorghum	70	[25]
Soybean	Clean grain storage with aeration	11–13	[21]
	Shelled grain	13	[22]
Sugar cane	Stalk (average)	75	[26]
	Top of the stalk	82.3	[27]
Sunflower	Clean grain stored with aeration	8–11	[21]
	Mature grain	~50	[28]
Switch grass	Dakota leaf type	9.84	[29]
	Columbus leaf type	13.27	[29]
Wheat	Clean grain stored with aeration	13–14	[21]
	Shelled grain	14	[22]

and fertilizer [66,67]. While the efficiency of anaerobic digestions is dependent of the water content in the feedstock, higher initial organic contents will lead to higher biogas production, as expected [68].

2.2. Water requirement for biomass processing

The availability of fresh water greatly determines the sustainability of the production of biomass. While the drought resistance properties of plants are one of crucial parameters during plant

selection, the water requirements for processing represent another important issue [69]. Depending on the climate, the usual rainfall can cover the main portions of the water requirements, but irrigation become crucial in dry seasons to maintain high yield and good quality. In general, various pre-treatment methods involving water have been practiced for most of the processing technologies including saccharification either with acids or bases, esterification, hydration/dehydration, and deoxydehydration.

Steaming with or without explosion can be performed mainly independently of the biomass' initial water content, therefore it is

Table 3
Water content of forestry and agricultural residues and food wastes.

Biomass wastes	Type	Moisture content (wt%)	Ref.
Forestry residues	Fresh	48.91	[10]
	Dry	8–10	[10]
	Bark	45–65	[35]
	Coniferous tree with needles	50–60	[35]
	Christmas tree in USA	37.81	[9]
	Fresh wood chips and sawdust	40–60	[36]
	Dry wood chips and sawdust	10–20	[36]
	Fresh wood chips	40–60	[36]
	Wood chips stored and air-dried	30–40	[36]
	Waste wood	10–30	[36]
	Yard waste, mostly wood chips	38.07	[37]
Agricultural residues	Corn leaf	8.11	[38]
	Corn stover	5–6.06	[39]
	Corn stalk	8.02	[14]
	Barley straw after harvesting, Canada	6.90	[40]
	Rape stalk, Finland	8.35	[41]
	Rice hulls	10.94	[42]
	Rice straw, Canada	7.5	[43]
	Rice straw	9	[44,45]
	Post-hydrolysis lignocellulose	13–20.6	[46]
	Sorghum bark, Greece	56	[25]
	Sorghum pith, Greece	77	[25]
	Sunflower stalks sundried after harvesting in India	9.20	[47]
	For forage and fermentation	12.9–15.70	[48,49]
	Wheat straw for gasification or energy	6.00–11	[50,51]
	Wheat straw as pellets	6.80	[52]
Mixed waste paper	8.75	[37]	
Sugar cane bagasse, Hawaii	10.39	[29]	
Food wastes	Average in the EU	70–80	[53]
	Average in the USA	72	[54]
	Dining halls in South-Korea	80	[55,56]

Table 4
Moisture content of different type of animal manure.

Type		Moisture (%)	Ref.	
Liquid manure/slurry	Cattle	87.7–99.5	[63]	
	Swine	84.8–99.51	[63]	
	Poultry	63.3–99	[63]	
Solid manure	Cattle	87.7–99.5	[63]	
	Swine	84.8–99.51	[63]	
	Poultry	63.3–99	[63]	
Phase not defined	Cattle	Dairy and beef	85.2–87.44	[61,62,65]
		Feedlot	78.39	[65]
	Poultry	Swine	72.3–75.4	[61,62]
		Chicken	79.3	[62]

Table 5
Composition of manure based on dry weight in weight %.

Type		Crude protein	Total amino acids	Total lignocellulose	Hemi-cellulose	Cellulose	Lignin
		%	%	%	%	%	%
Cattle manure	Dairy	18.1	7.92	52.6	12.2	27.4	13
	Beef	12.1	7.61	51.5	17.4	21.9	12.2
	Feedlot	17	10.89	41.7	21.4	14.2	6.1
Swine manure	Nursery	25.1	16.56	39.2	21.9	13.2	4.1
	Grower	22.7	18.99	39.1	20.4	13.3	5.4
	Finisher	22	15.63	37.4	21.6	12.9	2.9
Poultry manure	Chick starter	39.8	13.52	31.7	18.3	8.5	4.9
	Pullet grower	48.4	17.31	36.4	21.5	7.7	7.2
	17–40 Weeks post-polt diet	31.6	7.61	34.5	20.2	11.1	3.2
	Post-molt diet	28	10.61	31.2	16.4	10.7	4.1

Table 6
Water consumption in corn-based ethanol plants.

Water consumption (liter of water per 1 L of ethanol)	Year	Ref.
Average 5.8	1998	[77]
Range 1–11, (average 4.7)	2002	[78]
4.2	2005	[77]
4.1	2006	[79]
2.7	2008	[80]

a widely used pretreatment for both ethanol and biogas production [70]. The oldest hydrothermal pretreatment method is cooking of lignocellulosic materials in liquid hot water, used by the pulp industries [71]. The typical concentration of biomass could be between 6 and 20 wt% [72]. Due to poor reproducibility, the suggested biomass content should be below 5 wt% involving much higher volume process water. For steam pretreatment the pressure and temperature of steam could be adjusted and the biomass concentration usually 50 wt% [71].

Alkaline pre-treatment of lignocellulose usually uses 1–2 wt% NaOH solution [73] or 10 wt% ammonia liquor [74] to solubilize the hemicellulose components.

Considering acid catalyzed hydrolysis, sulfuric acid is the most commonly applied acid, though the use of other acids such as HCl and nitric acid was also reported for all kind of biomass' water content [75]. The acid pretreatment can operate either under a high temperature and low acid concentration or under a low temperature and high acid concentration. [76].

The development of more efficient technologies with respect to the water consumption can be demonstrated by the production of corn-based ethanol using first generation bio-ethanol technology (Table 6). Early data regarding water consumption

in ethanol plants reveal values in the range from 1 to 11 L of water per a liter of ethanol. Water requirements of the production process could be decreased by energy integration and water optimization including water recycling and zero discharge. By this

optimization method the water consumption should be 2.85 L of water per 1 L of ethanol [81]. The application of dry mill technologies further decreased the water demand [80]. By 2008, the water requirement of corn ethanol could be decreased to less than the half of the demand of 1998. A recent study has demonstrated the importance of water recycling by using either un-treated or purified grey water (e.g. process water) or green water (e.g. rain water). In this way the consumption of blue water (e.g. fresh water) can be significantly reduced in bio-fuel production technologies [82]. A state-of-the-art corn-based plant could operate with as low as 1.5 L water per liter ethanol demand [83].

Pacific Northwest National Laboratory developed a fast-pyrolysis plant applying hydro-treating and hydrocracking, which would use 2000 dry metric tons/day of hybrid poplar wood chips to produce 320 million liters/year of gasoline and diesel with an estimated water requirement of 3.0 L water for a liter product. Cooling water represents most of water demand, since it is recirculated in the quench system, therefore resulting in a low value [84].

Consumptive water usage in the biochemical conversion process is generally considered to be high compared with a thermochemical conversion process. The biochemical conversion of corn stover was simulated and optimized by researchers in National Renewable Energy Laboratory and a competitive value of 5.4 L water per liter product was revealed [85].

Water management is a crucial issue in biomass processing technologies and a necessary tool to secure low water consumption in the future.

2.3. Water as a reaction medium

Water is a cheap, readily available, nonflammable, non-toxic, and therefore one of the greener solvents. It is especially suitable for reactions involving ionic species, since the water molecules can readily solvate both the anions and cations. Water can serve both as a solvent and a ligand resulting in the reversible coordination to

Table 7
Formation of levulinic acid from C₆ and C₁₂ sugars.

Entry	Source	Acid	Temp (°C)	Yield (mol %)	References
1	D-Fructose	HCl (2 M)	170	49	[99]
2	D-Fructose	H ₂ SO ₄ (1.8 M)	170	42	[99]
3	D-Glucose	HCl (1.8 M)	170	48	[99]
4	D-Glucose	H ₂ SO ₄ (2 M)	170	40	[99]
5	Sucrose	H ₂ SO ₄ (1 M)	125	30	[100]
6	Sucrose	H ₂ SO ₄ (1.8 M)	140	35	[101]
7	Sucrose	HCl (2.8)	125	43	[99]
8	Sucrose	HBr (1 M)	125	50	[99]
9	Cellobiose	HCl (2 M)	170	46	[99]
10	Cellobiose	H ₂ SO ₄ (2 M)	170	34	[99]

Table 8
Production of levulinic acid from various biomass resources.

Entry	Source	Acid	Temp (°C)	Yield (wt%)	References
1	Cellulose	HCl (2 M)	170	31	[99]
2	Cellulose	H ₂ SO ₄ (2 M)	170	23	[99]
3	Chitin	H ₂ SO ₄ (2 M)	190	21.6	[99]
4	Olive tree pruning	HCl (10 M)	200	18.6	[102]
5	Sweet sorghum	H ₂ SO ₄ (2 M)	160	31.4	[103]
6	Poplar sawdust	HCl (10 M)	200	21.3	[102]
7	Wheat straw	HCl (10 M)	200	19.3	[102]
8	Tobacco chops	HCl (10 M)	200	5.2	[102]
9	Tobacco chops	H ₂ SO ₄ (5 M)	200	3.7	[102]
10	Water hyacinth	H ₂ SO ₄ (1 M)	175	3.5	[104]
11	Wood sawdust	HCl (0.5 M)	190	9	[105]
12	Starch	HCl (0.5 M)	200	49	[106]
13	Corn starch	HCl (1.8 M)	162	37	[107]
14	Pulp slurry	HCl (1.8)	160	65	[108]
15	Sorghum grain	H ₂ SO ₄ (0.8 M)	200	32	[99]

[96]. Its bisphenol derivative could be a substitute of bisphenol-A in polymer manufacture [94].

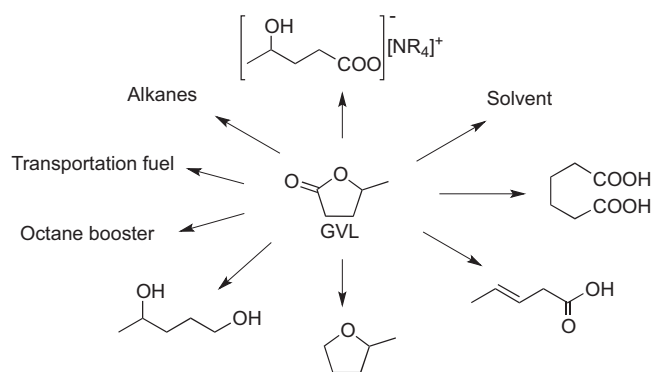
The first synthesis of LA from saccharose in the presence of aqueous HCl was reported by Mulder in 1840 (Scheme 4) [97].

It is important to emphasize that the theoretical yield of LA formation from C₆-sugars is 68.7%. However, the experimental yields are commonly less than the theoretical one due to the formation of humins and/or tar as by-products. The yields of LA from C₆ and C₁₂ sugars were reported to be between 30 and 50% in the presence of sulfuric or hydrochloric acids; however the latter is more efficient under aqueous conditions (Table 7). Moreover, higher yields could be usually obtained by hydrolyzing feedstock with a higher content of C₆-sugars, such as starch or pulp slurry, at high temperatures, as expected (Table 8).

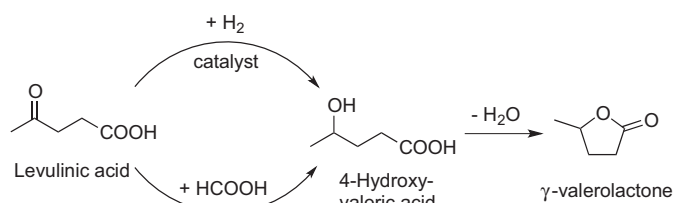
Another important derivative is γ -valerolactone (GVL), which can readily be obtained by the reduction of LA and has been proposed as a sustainable liquid and fuel [108]. It can be used for the production of transportation fuels, butane isomers [109], octane booster [108], alkanes [100], 2-methyl-tetrahydrofuran [100], pentane-1,4-diol [100,110], ionic liquids [111,112], adipic acid [113], alkyl valerates [111], polymers [114], pentanoic acid [115] or utilized as a solvent [116,117] (Scheme 5).

Since LA is soluble in water, several aqueous systems were developed for the hydrogenation of its carbonyl group that leads to the formation of 4-hydroxyvaleric acid (4-HVA). The latter could readily undergo dehydration to form GVL (Scheme 6). It is important to note that water does not form azeotropic mixture with GVL, thus it can be isolated by simple distillation [108]. Since the increasing importance of GVL, several homogeneous and heterogeneous catalytic systems have been developed successfully for its production.

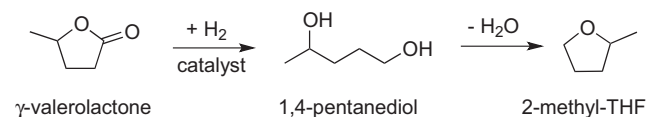
The first application of water-soluble homogeneous HRuCl(PPMS)₃ catalyst for the reduction of oxo- and keto



Scheme 5. GVL based chemicals.

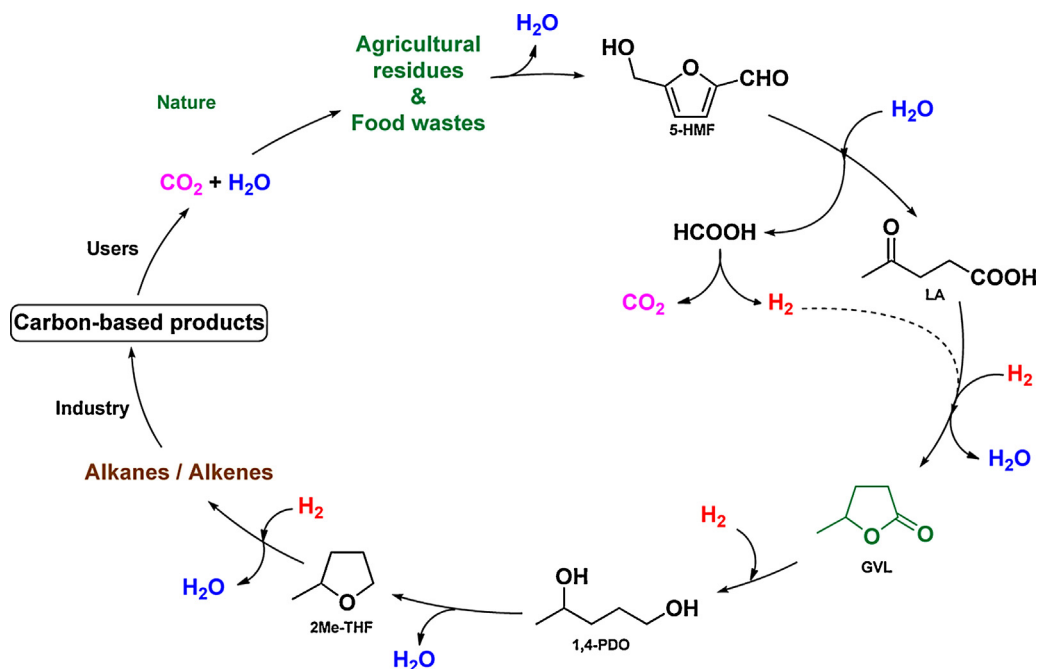


Scheme 6. Reduction of LA to GVL.



Scheme 7. Conversion of GVL to oxygenates.

acids was reported by Joó et al. years before others [118,119]. However, the catalytic activity was low (TOF = 13 h⁻¹) at pH = 1. It was shown that LA could be converted to GVL by the use of Ru/TPPTS catalyst in aqueous solution with 95% yield at 140 °C [100]. The application of TPPTS modified Ru catalyst in biphasic hydrogenation of LA in CH₂Cl₂/H₂O was reported by Heeres et al. resulting in excellent yields under mild conditions; however the conversion was significantly lower (55%) in the second run of the recycling [120]. Kühn et al. tested the series of water soluble Ru catalyst formed *in situ* from RuCl₃ or Ru(acac)₃ and water soluble phosphines such as PTA, TXPS or TPPS. By the use of catalyst loadings of 0.2 mol%, the product yields were up to 99% conversion with selectivity of 97% along with a maximum TOF = 200 h⁻¹ using TPPTS ligands at 140 °C. A ruthenium phosphine complex immobilized on the amphiphilic copolymer PS-PEG was also examined under the same conditions and gave 90% conversion of LA [121]. Recently, much more active (TOF = 2160 h⁻¹) iridium complexes with 2,2'-bipyridine ligands were reported for the hydrogenation of LA under mild conditions in water using [LA] = 1 mol dm⁻³ initial concentration [122]. However, in spite of the high activity, the final product concentration is less than 1 M and the water-removal step could result in low energy efficiency of the process. It should be noted, that during the catalyst recycling the decrease of GVL yield was negligible for five consecutive runs. It was recently reported that the reduction of LA can be performed under solvent free conditions – the reaction can be initiated in neat LA in the presence of catalyst *in situ* formed from Ru(acac)₃ (0.016 mol%) and 10 fold excess of (C₄H₉)₃P(C₆H₄-*m*-SO₃Na)₂ ligand under 10 bar of H₂ at 140 °C resulting in TOF of 3540 h⁻¹ [123]. The *in situ* IR investigation established that the catalyst still remained active after full conversion of LA. The efficiency of the Ru catalyst



Scheme 8. Multistep conversion of carbohydrates to carbon-based products.

operating under solvent free conditions was further increased up to $\text{TOF} = 21,230 \text{ h}^{-1}$ by the application of bidentate $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ ligand at 160°C [124].

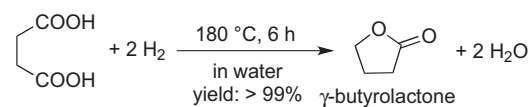
It should be noted that the catalytic transfer hydrogenation of LA in the presence of formic acid and the Shvo-catalyst was reported as an alternative, external hydrogen-gas independent route for the production of GVL [125].

Heterogeneous catalytic systems are mainly operated by using supported transition metal catalyst such as Pd/C, Ru/C, Ru/SiO₂, Ru/TiO₂, Ru/Al₂O₃ or Raney-Ni under 1–250 bar H₂ at 70–265 °C. Although these catalysts can easily be separated from the reaction mixture, the activity and selectivity are far from the homogeneous ones, as expected [126]. Moreover, these systems do not use water as a solvent, but usually contain co-solvents e.g. alcohols, which may cause separation difficulties [127]. The continuous hydrogenation of aqueous solution of LA to GVL was also reported using H-Cube® and H-Cube Pro™ flow reactors, which generates hydrogen gas *in situ* by the electrolysis of water, then continuously mixed with the substrate. When Ru/C was used as catalyst bed in the CatCart®, conversion exceeded 97% with 100% of selectivity at 1 mL/min flow rate at 100°C [128].

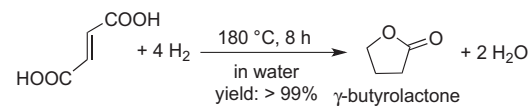
The subsequent reduction of GVL to 1,4-pentanediol and 2-methyl-THF (Scheme 7) and then to C₄, C₅, C₈ and C₉ alkanes was also demonstrated by the use of Ru and Pt-based catalyst systems [100]. Thus, the integrated conversion of the carbohydrate components of agricultural residues and food wastes to value added carbon-based consumer products was demonstrated (Scheme 8) [100].

Succinic, fumaric and maleic acids were identified as C₄-platform chemicals [87]. For example, succinic acid can be produced by fermentation of carbohydrates and used as a feedstock for the production of pharmaceuticals, 1,4-butanediol, γ -butyrolactone, surfactants and detergents, biodegradable plastics, and ingredients to stimulate animal and plant growth [129]. It has been used for the beverage industry primarily as an acidity regulator for decades. Fumaric acid has been also used as a food additive and it has an important role in the manufacturing the polyester resins.

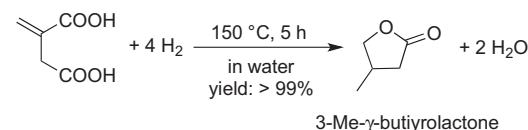
An aqueous reduction of succinic acids using syngas (Scheme 9) was developed [130]. The conversions were found to be excellent



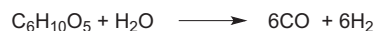
Scheme 9. Conversion of succinic to γ -butyrolactone.



Scheme 10. Conversion of fumaric to γ -butyrolactone.

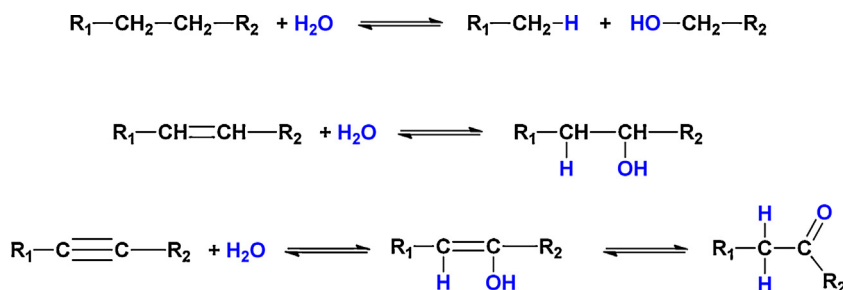


Scheme 11. Hydrogenation of itaconic acid to 3-methyl- γ -butyrolactone.



Scheme 12. Cellulose gasification by steam reforming.

in the presence of Au/*m*-ZrO₂ heterogeneous catalyst operating 20–50 bar at 120°C . The fastest reduction was achieved, when the partial pressure of hydrogen was higher. Although, the product conversion and selectivity was not affected by the CO:H₂ ratio, the reaction time was longer at lower $p(\text{H}_2)$, expectedly. The catalyst was successfully applied for the reduction fumaric acid, as well. When itaconic acid or lactic acid was reduced the conversions and selectivity were found to be 100% and >87% for the formation of 3-methyl- γ -butyrolactone and 1,2-propanediol, respectively (Schemes 10 and 11).



Scheme 13. Hydrolysis, hydration, and dehydration reactions.

Syngas (CO+H₂) and biogas (CH₄+CO₂) are the potential C₁-products of biomass conversion. While biogas is produced by meso- or thermophilic microorganisms at moderate temperature through anaerobic digestion [131], syngas is formed at elevated temperatures by the gasification process. Gasification can be carried out in air, pure oxygen and/or steam media generating a gaseous product containing CO, H₂, CO₂, CH₄ and N₂ in various proportions [132]. According to Corma, gasification can be carried out in three different ways: partial oxidation (in presence of air), pyrolysis (absence of oxygen), and steam gasification [133]. Of the gasification routes listed on (Scheme 12), steam gasification requires significant amount of water in a form of steam. The product composition depends on the ratio of water.

New approaches of co-gasification of biomass and coal, or partial oxidation and steam reforming of biomass pyrolysis oils were suggested for syngas production and higher H₂/CO ratio could be achieved by using biomass-derived char technology. An alternative option for syngas generation is the coupled steam hydrogasification of biomass and reforming of methane [134].

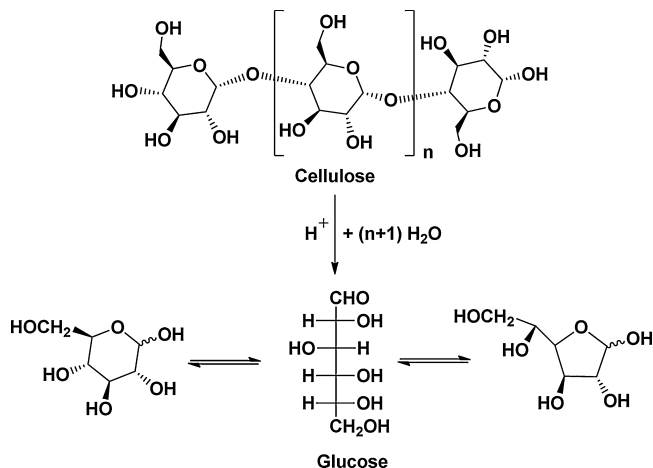
2.4. Fundamental reactions involving water

Hydrolysis, hydration, and dehydration reactions are the most important transformations involving water (Scheme 13). In the case of carbohydrates, these reactions are usually reversible and could follow each other in the presence of catalysts leading to the formation of a wide range of products.

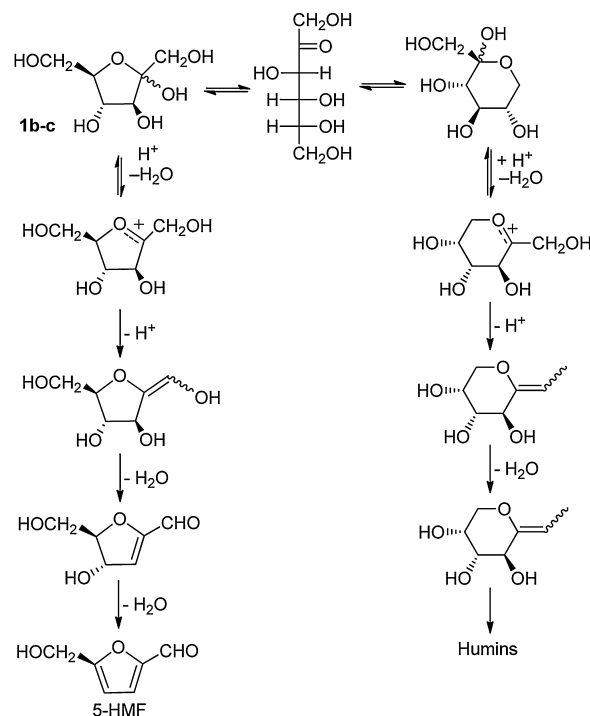
Cellulose is one the most abundant carbohydrates on the Earth consisting of D-glucose units connected by β(1→4) bonds. The seminal work of Payen in 1839 described the main constituents of wood with the empirical formula of C₆H₁₀O₅, which was named to cellulose [135]. The currently accepted structure of cellulose (Scheme 14) was given by the Nobel-laureate Staudinger in 1922 [136]. The utilization of cellulose as a renewable resource has been

around for a long time. Several processes have been developed for the acid catalyzed dehydration of cellulose for the production of simple sugars that can be fermented to value added products. Typical operation conditions are as follows: 25–240 °C in the presence of HCl, H₂SO₄, and HF. The mechanism of the hydrolysis of cellulose, which follows a similar pathways as acid catalyzed decomposition of glycosides to glucose was summarized by Schüth in a recent review [137].

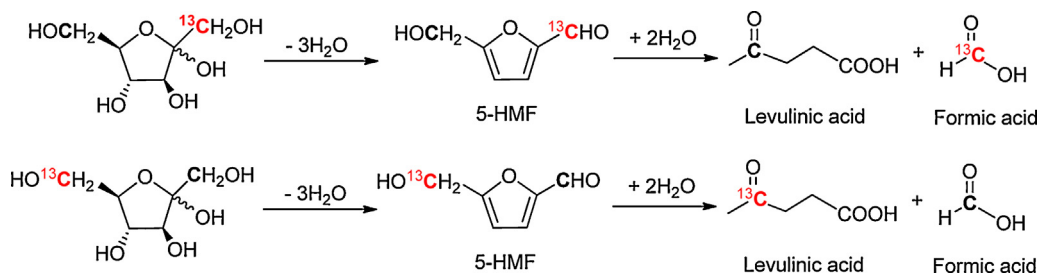
The dehydration of carbohydrates to 5-HMF has also been studied for decades [138]. It is well established that the 5-HMF yields are rather low in water and many by-products called “humins” are formed. The solvent dependence of the acid catalyzed dehydration of fructose to 5-HMF has been observed by *in situ* NMR [89,139]. It was shown that the yield of 5-HMF was the highest in DMSO or THF. The nature of the acid and its concentration is another important factor in the production of 5-HMF [139]. Riisager has developed a novel technique for the synthesis of 5-HMF under aqueous conditions in the presence of HCl as catalyst resulting in a modest yield of 32%, which can be increased by using short contact time (1 s) at high temperatures (200 °C) [140]. The molecular map of the conversion of fructose to 5-HMF using ¹³C-labeling technique as well as a detailed *in situ* characterization of intermediates was reported in 2012 [139]. It was established, that the preferred path of the dehydration proceeds through the fructofuranose isomers (Scheme 15).



Scheme 14. Conversion of cellulose to glucose.



Scheme 15. Conversion of fructose to 5-HMF.

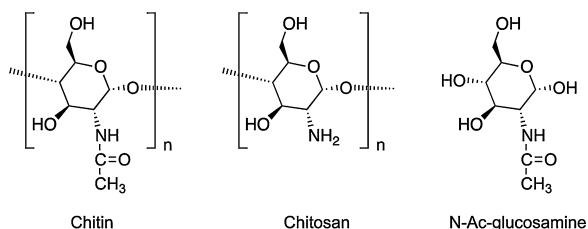


Scheme 16. Conversion of 5-HMF to levulinic and formic acid.

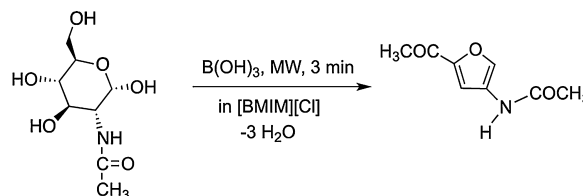
Series of metal halides in 1-alkyl-3-methylimidazolium chloride were found to be an efficient catalysts for the conversion of monosaccharides to 5-HMF, among which chromium (II) chloride was the more efficient resulting in nearly 70% yield from glucose [141]. It should be noted that only negligible amount of LA was formed. The metal free dehydration of D-glucose and its polymeric forms to 5-HMF were investigated in several solvents including imidazolium based ionic liquids, DMF, and DMSO by the use of boric acid as catalyst [142]. A yield up to 42% from glucose and 66% from sucrose was achieved in [BMIM][Cl] at 120 °C, significantly higher than by the use of DMSO (13%). Although, that yields were not higher than that of obtained in the presence of chromium catalysts (70%) [141], it represents a new class of promoter for the production of 5-HMF.

The first mechanism of the hydration of 5-HMF to the equimolar mixture of levulinic and formic acids was reported in 1985 [143]. A similar study reported for DMSO and H₂O has verified that the C₁- and C₆-carbons of D-fructose appears at the corresponding position in 5-HMF [144], which was transferred into the formic acid and the carboxyl group of the levulinic acid, as expected (Scheme 16).

Chitin is the second most abundant biopolymer after cellulose on the Earth (Scheme 17). It is available from the exoskeletons of crustaceans such as crabs, lobsters, shrimps, and in the cell walls of fungi. Although, its formation is exceeded 100 billion tons annually [145,146], the utilization is around 150,000 tons/year [147]. Accordingly, the efficient transformation of this N-containing polymer or its derivatives e.g. chitosan and N-Ac-D-glucosamine (Scheme 17) could be another route for the production of carbon based building blocks and nitrogen containing compounds. Accordingly, the microwave-assisted acid catalyzed hydrolysis was investigated in the presence of both hydrochloric and sulfuric acids resulting in 19–27 wt% yield of levulinic acid depending on the substrate [98]. These reactions require slightly higher temperatures than that of applied for the efficient conversion of lignocellulose or starch. The microwave-assisted conversion of chitosan was also studied in the presence of different of Lewis-acid catalyst in water at 200 °C [148]. The most efficient catalyst was SnCl₄ resulting in 24 wt% of LA. High 5-HMF selectivities were obtained by the use of different triflates e.g. La(CF₃SO₃)₃ or Yb(CF₃SO₃)₃ and iron perchlorate, however, the yields were below 10%. When the exoskeleton of



Scheme 17. The structure of chitin, chitosan, and N-acetyl-glucosamine.



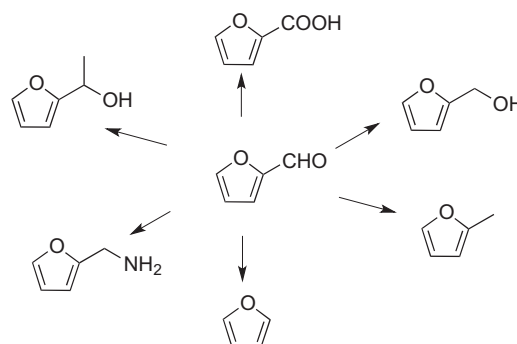
Scheme 18. Synthesis of 3-acetamido-5-acetylfurane.

crab and shrimp was treated at 200 °C, the reactions were selective for LA with average yield of 12.6 wt%.

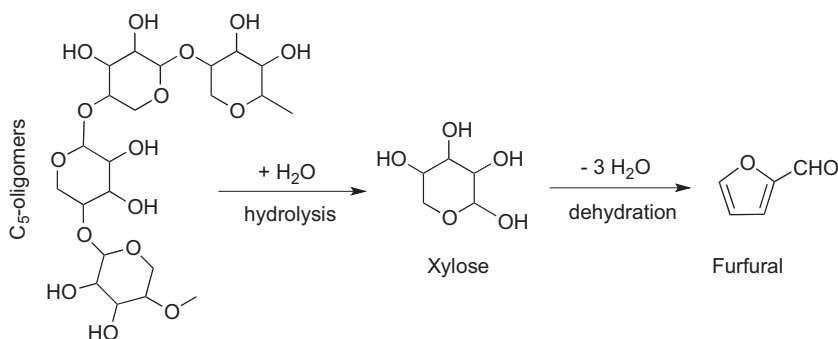
The direct conversion of N-acetyl-D-glucosamine *via* dehydration reaction to 3-acetamido-5-acetylfurane was also investigated in several ionic liquids between 120 and 180 (Scheme 18) [149]. It could be a precursor of polyamide proximicines [149] that are isolated from *Verrucosipora*, a marine actinomycete. The product formation could be accelerated by the addition of different additives – the highest yield of 60% was achieved when boric-acid was used in 10 mol% concentration in [BMIM][Cl] at 180 °C. The kinetic study of the reaction revealed that the activation energy was 82.8 kJ/mol [150]. The yield can slightly be increased by the addition of NaCl and the application of higher temperature (220 °C) [151].

Furfural is another C₅-platform chemical [152], which can be used for the production of basic chemicals, fuel additives, solvents, etc. (Scheme 19).

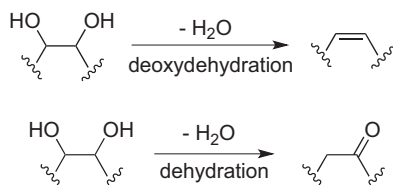
Furfural is currently produced from xylose, which can be obtained from hemicellulose *via* acid catalyzed hydrolysis [152,153]. The application of simple acid-functionalized pyridinium- and ammonium based ionic liquids for the one pot production of furfural from xylose was recently reported [154]. High (>90%) xylose conversions and furfural yields (>70%) were obtained, when 1-(4-sulfonylbutyl)-pyridinium methanesulfonate was used as catalyst at 150–180 °C using microwave irradiation at 100 W for 1 h. The catalyst system was also successfully utilized for the treatment of lignocellulosic waste derived C₅ syrup produced



Scheme 19. Furfural based chemicals.



Scheme 20. Conversion of C₅-oligomers to xylose and furfural.



Scheme 21. Competing reactions: deoxydehydration and dehydration.

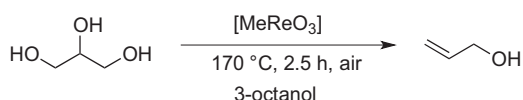
from cereal straws containing a mixture of sugar monomers (xylose and arabinose, 12%), oligomers (30–35%) and other impurities *e.g.* proteins, waxes, minerals up to 20%. It was found that the maximum furfural yield of 30% could be achieved in 30 wt% aqueous solution at 150 °C for 2 h. The catalyst containing aqueous phase was separated and reused resulting in same yield in the first run; after which the activity decreased significantly to 14% in the second catalyst recycle.

A non-catalytic microwave-assisted hydrothermal conversion of xylose to furfural resulted in a moderate yield of 49% at 200 °C (Scheme 20) [155]. The conversion of xylan required lower temperatures (160–180 °C) in order to promote the hydrolysis of the polymer and C₅-oligomers, yielding xylose instead of furfural.

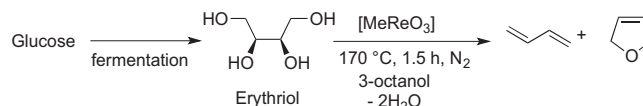
One of the elegant approaches of the oxygen-rich carbohydrate utilization for the production of simple organic molecules is the deoxydehydration reaction, which eliminates two adjacent –OH groups from vicinal diol to produce an olefin (Scheme 21). It is important to note that dehydration is a competing transformation leading to a carbonyl compound.

It was demonstrated that various rhenium carbonyls *e.g.* [Re₂(CO)₁₀, BrRe(CO)₅, (Cp*₂Ru₂(CO)₂]₂] can deoxygenate diols and epoxydes either in the presence [156] or the absence of secondary alcohol as solvent/reductant [157] or by the use of H₂ [158]. MeReO₃ [159] can efficiently convert several bio-derived diols or polyols to valuable chemicals under air or N₂ at 170–200 °C. Glycerol, which produced in large quantities as by-product of biodiesel production, was converted to allyl-alcohol with excellent yield (90%) (Scheme 22).

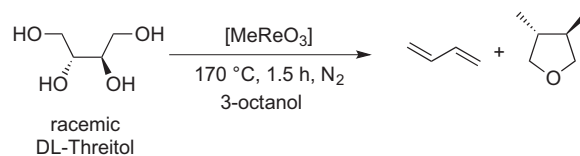
The C₄ sugar alcohol erythriol, which can be obtained by the fermentation of glucose [160] or by the decarbonylation of pentoses [161], was converted to 1,3-butadiene in 89% along with 11% 2,5-dihydrofuran as the by-product (Scheme 23) and neither 1,4-anhydroerythriol nor unsaturated alcohols were formed. When racemic DL-threitol was subjected to deoxygenation under identical



Scheme 22. Conversion of glycerol to allyl-alcohol.



Scheme 23. Glucose based synthesis of 1,3-butadiene *via* erythriol.



Scheme 24. Deoxygenation of racemic-threitol.

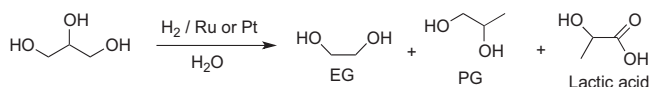
conditions, 1,3-butadiene was obtained with similar yields, however racemic mixture of 1,4-hydroerythriol was formed instead of 2,5-DHF (Scheme 24). The use of MeReO₃ was successfully extended to the conversion of C₅-sugar alcohols, such as xylitol, to 1,3-diene ether derivatives. If D-sorbitol or D-mannitol were used as the C₆-sugar alcohols, deoxydehydration resulted in *E*-hexatriene in moderate yield (54%).

Interestingly, when different inositol isomers were treated under similar conditions, the mixture of benzene and phenol was obtained in yields between 24–96%. It should be noted, that the conversion of higher alcohols requires higher temperature (200 °C) than that of applied for either diols or glycerol.

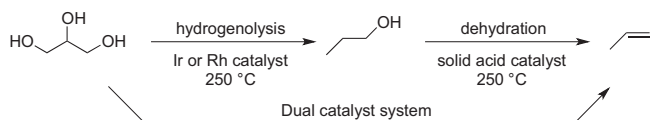
The hydrogenolysis of polyols such as glycerol is one possible route for the production of oxygenated chemicals including ethylene glycol (EG), propylene glycol (PG), and lactic acid. EG and PG have industrial importance for the production of polymers, resins, foods, cosmetics, and functional fluids (antifreeze, deicing). Although, lactic acid and its salts have relevance in the food and beverage industry, the greatest opportunity for the use of lactic acid is the production of polylactic acid. The efficiency of heterogeneous supported transition metal catalysts for the hydrogenolysis of polyols to lower molecular weight glycols and acids have been demonstrated by several studies [162–165]. Furthermore, the addition of base has been reported to enhance the conversion of polyols [166]. For the mechanism of hydrogenolysis of glycerol both glyceraldehyde-based [167] and dehydration–hydrogenation mechanism have been proposed [168].

Transformation of glycerol to EG and PG glycol was studied by the use of carbon-supported Ru and Pt catalysts under 40 bar H₂ at 200 °C – ruthenium was more active than platinum at neutral pH. Ru-based catalysts favored the formation of EG over PG but also catalyzed the formation of methane. The less active Pt catalyzed propylene glycol formation with high selectivity (Scheme 25) [169].

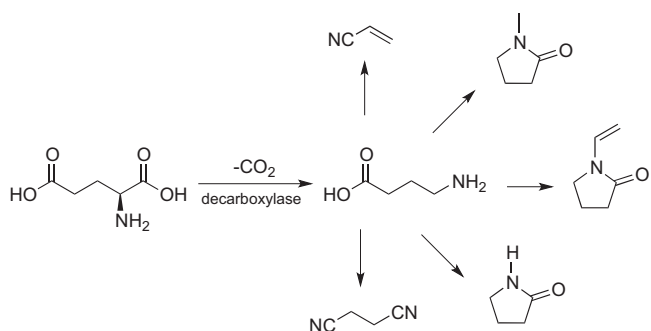
The conversion of xylitol to EG/PG as main products was reported in the presence of supported Ru catalyst on activated



Scheme 25. Deoxygenation of glycerol to glycols.



Scheme 26. Production of propylene from glycerol.

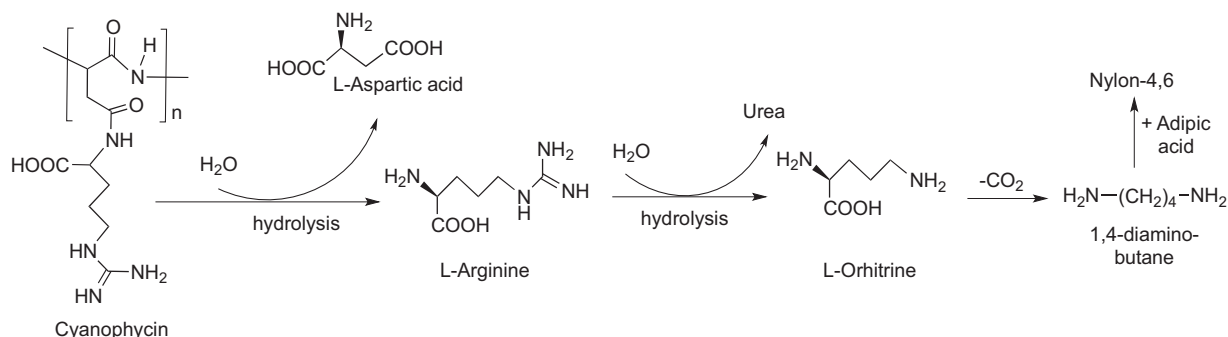


Scheme 27. Utilization of glutamic acid-based gamma-aminobutyric acid.

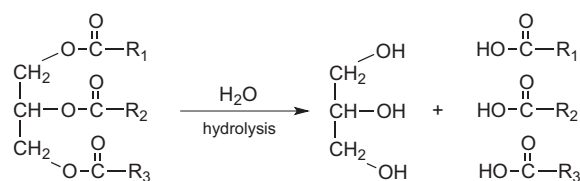
carbon (Ru/C) or on metal oxides (Ru/Al₂O₃, Ru/Mg₂AlO_x, Pt/C etc.) under aqueous conditions in the range of 1–10 bar H₂ and 140–260 °C. The maximum selectivity for glycols were obtained at 20–40 bar H₂ and 200–220 °C. Interestingly in the absence of hydrogen, lactic acid was detected as the main product. The selectivities could be also influenced by the addition of bases such as Ca(OH)₂ or Mg(OH)₂. Moreover, no significant decreases in the activity and selectivity were found, when Ru/C was recycled for six consecutive runs (Scheme 26) [170].

The two-step conversion of glycerol to 1-propanol and propylene was recently reported. The first hydrogenolysis step utilized metal-oxides- and carbon-supported Ir and Rh catalysts followed by dehydration over various solid acid catalysts. Direct conversion of glycerol into propylene over Ir/ZrO₂ coupled with HZSM-5-30 was successfully achieved [171].

Important chemicals could be obtained by the conversion of proteins [172]. For example, the hydrolysis of many plants and animal proteins could result in glutamic acid, the most abundant, non-essential amino acid [173]. The most important derivatives of glutamic acid are γ -aminobutyric acid [174], *N*-vinylpyrrolidone and *N*-methylpyrrolidone [175], acrylonitrile [176], and succinonitrile (Scheme 27) [177]. Similarly, *L*-lysine could have an important



Scheme 28. L-Arginine based synthesis of 1,4-diaminobutane.



Scheme 29. Hydrolysis of triglycerides.

role on the biomass based production of 1,5-diaminopentane [178], caprolactam [179] and 5-amino-valeric acid [180].

The selective hydrolysis of *L*-arginine to *L*-ornithine was performed by the use of *Bacillus subtilis* arginase in a continuously stirred membrane reactor system resulting in an outstanding activity (TON = 1.13 × 10⁸) at pH of arginine free base 11.0. It can be further increased to TON = 10⁹ by the addition of sodium-dithionite to the substrate solution [181]. It was demonstrated that the hydrolysis of *L*-arginine to *L*-ornithine and urea could be a key step in the biomass-based production of 1,4-diaminobutane, a monomer of nylon manufacture. *L*-arginine has become a widely available resource from biomass waste streams via the nitrogen storage polypeptide cyanophycin (Scheme 28).

Fatty acids that include all saturated and unsaturated aliphatic carboxylic acids with carbon chain lengths in the range of C₆–C₂₄ can be applied in various sectors of industry as the acids themselves or in the form of derivatives e.g. esters, alcohols, soaps, detergents, amides [182]. Accordingly novel strategies for greener production of biodiesel and platform chemicals from second generation triglyceride feedstocks such as non-edible plant oils, algal oil or waste cooking oils and fats – have come to focus of interest. The catalytic hydrolysis produces a mixture of glycerol and fatty acids (Scheme 29).

Currently, they are produced from the reaction of oils and/or animal fats using superheated steam. Typically, the reactions are carried out at 100–260 °C and 1–70 bar using a 0.4–1.5 wt% water-to-oil ratio [183]. Different variations of this technology have been used by industry and are normally referred to as fat splitting [182,184–187]. The use of a subcritical water, which can act as both solvent and reagent for the hydrolysis of triglyceride [183,188], has been proven to be effective for hydrolyzing soybean oil to free fatty acids resulting in rapid splitting of triglycerides at temperature range of 330 and 340 °C yielding 97% or higher conversion without the need of catalysts or emulsifying agents [184]. The subcritical water-assisted splitting was also reported – the conversion of the esters to free fatty acids exceeding 95% was achieved at 340 °C [189]. The application of IR study on the hydrolysis revealed structural changes in the chains of the unsaturated fatty acids and their partial polymerization during the hydrolysis.

3. Conclusion

Water can have many different roles in catalytic biomass-based technologies to produce chemicals and fuels. First and foremost, water is one of the two basic chemicals of nature used during photosynthesis to produce biomass. Consequently, biomass contain different amounts of water, which can be advantageously utilized during the conversion schemes. Water could be the solvent of the reactions or just either the eliminated product or the reactant resulting in hydration and hydrolysis. Since some of these roles are intrinsically part of the natural system, their change could be very difficult or even not possible. Therefore, the designer of the chemistry or the process must understand the possible roles of water at the molecular and macroscopic levels, which indeed requires a genuine collaboration of biologists, chemists and engineers.

Acknowledgments

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