Recent advances in the catalytic production of platform chemicals from holocellulosic biomass via hydrolysis

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Abstract: This review discusses the novel catalytic pathways of lignocellulosic biomass to value-added chemicals, such as biomass-derived sugar alcohols, organic acids, furans and biohydrocarbons. These production approaches are undertaken by biological, chemical and thermochemical transformations or a combination of them. Nevertheless, the majority of the research is focused on developing heterogeneous catalytical systems to convert value-added products from holocelluosic biomass. Biorefineries represent the peak of biomass processes in order to produce valuable chemicals and liquid fuel components avoiding the utilization of corroding and toxic elements. The main objective of the present review is to offer the reader a broad overview of recent holocellulosic-based chemical and fuels production technologies via heterogeneous catalysis. There is also an overview of the economic aspects to efficiently produce these platform chemicals on an industrial scale. To summarize this review, an outlook and conclusions of catalytic processes are highlighted.

Contents

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1. Introduction

Biomass is the only renewable resource that can sustainably meet our needs for the production of fuels, chemicals and materials.[1] An average of 1466 Mt of total terrestrial biomass (dry matter) was produced annualy from 2006 to 2015 and 1.5 Mt (dry weight) from fisheries and aquaculture in the European Union (EU).[2, 3] Lignocellulosic biomass refers typically to plant-based biomass (such as corn stover, straw, forestry and agricultural residues) and it is the most abundant (after atmospheric CO_2) and inexpensive carbon source. Thus, it has been found to be a valuable commodity due to its scalability, economic viability and its potential carbon neutrality. These convenient aspects converge in the production of renewable biofuels and value-added products via appropriate technologies. These plant biomass resources are diverse, and only a small part of these raw materials is efficiently used. Hence, there exists a need to establish innovative, environment-friendly processes and cost-effective perspectives to benefit from these resources.[4]

Pursuing the same philosophy, an industry that is able to conceive efficient catalytic biomass conversion would accomplish the complete employment of the plant matter feedstock into useful chemicals, fuels and energy. To achieve these goals, biorefineries play a dominant role by carefully selecting biomass derivates (platform molecules or building blocks). The biorefinery concept envisages a path to products from biomass via platform molecules. Originally, the United States Deparment of Energy (USDOE) stressed the 12 most relevant platform molecules as the key starting materials on which to focus future research endeavors. These compounds have gained a valuable niche among industry and academia within the past decade, due to its effective-development environmentally-benign technology, and offering a solution to agricultural and forestry waste.[5]

Significant transformations of biomass into valuable organic acids incorporating fumaric, itaconic, lactic, levulinic, succinic, and polyols – were included as examples in the orginal NREL list.[6] Years later, Bozell and Petersen revisited this list and included building blocks (e.g. ethanol, furfural and succinic acid) on which the present review is based.[7] A presentation from the USDOE in collaboration with Virent Inc. claims that a significant share of biomass (corn stover, loblolly pine and sugarcane bagasse) is transformed into fuels and high value aromatic chemicals.[1] These valuable compounds can be formed via pyrolysis and gasification, and via fermentation or chemo-catalytic routes, respectively.

Lignocellulosic matter is primarily constituted by cellulose, hemicellulose and lignin.[10-19] Holocellulose considers cellulose and hemicellulose (the carbohydrate part of lignocellulose). Hemicellulose is formed by pentoses (xylose, arabinose and ribose) and hexoses (glucose, fructose, galactose and mannose), of which xylose, a monomer of xylan, is the most common component.[20, 21] Hemicellulose is linked to cellulose by hydrogen bonds and it is more easily hydrolyzed than celluloses. Cellulose is a linear homopolymer consisting of glucosyl units bridged together through (1→4) glycosidic linkages;[22] these linkages include hydroxy groups that promote hydrophilic nature. Cellulose is the most abundant natural polymer on the planet. Its structure delivers lignocellulose with a high degree of strength to the wall and chemical complexity, which hinders its isolation from lignin and hemicelluloses.[23] Nevertheless, its chemical nature also provides the opportunity for modification and conversion into other valuable derivatives. Lignin is another main component of the lignocellulosic biomass. It is a three-dimensional polyphenolic biopolymer, which is formed inside the cell wall with a randomized distinctive structure that contributes, with rigidity and recalcitrance, to pretreatment techniques. However, its selective conversion into chemically useful applications remains a challenge.[24-26] Methoxy and phenol groups are the major functional groups in lignin.[27]

Moreover, hemicellulose-derived compounds (xylan and xylose) have not yet been completely valorized. At present, the pulp and paper industry mix a significant part of C_5-sugar-rich streams with lignin derivates, which are burned to obtain energy (used as process heat).[28] Nevertheless, the valorization of this stream is of major interest.

Catalysts play a key role in the efficient conversion of biomass in the chemical industry. They are defined as "a substance that changes the velocity of a reaction without itself being changed in the process".[29] It lowers the activation energy of the reaction but, in so doing, it is not consumed. Every year there are worldwide sales values of solid catalysts of approximately 13 billion €/ year, which create an added-value about 100 to 1,000 times higher. Molecules with catalytic activity or enzymes are also used as catalysts. Nevertheless, solid catalysts are preferred in a wide range of industrial applications due to their reusability potential and lower toxicity, among other advantages. From 80% to 85% of the current industrial processes use solid catalysts of some kind.[30]

1.1. Scope of the review

In recent decades, catalytic conversion of biomass derivates to value-added chemicals and fuels as a sustainable feedstock has been focused on with great interest. Gasification, pyrolysis and hydrolysis are the three main routes used to transform biomass into value-added materials.[31-35]

In this review article, we mainly focus on hydrolysis processes and hydrolysis-related processes used to break down the lignocellulosic biomass. This review excludes gasification and pyrolysis. Carbohydrates found in cellulose and hemicellulose can be hydrolytically converted into platform molecules, i.e. pentoses and hexoses found there, which can be employed afterwards as a feedstock for chemocatalytic conversion into polyols, furans and acids. For certain platform molecules, such as organic acids and polyols, biochemical paths are more developed than heterogeneous catalysis. Therefore, these production routes are included in the present review. Lignin derivatives are omitted from this study. Further applications for these platform chemicals are also reviewed. However, since the present review focuses mainly on the production of platform molecules, the further step of synthesis of their derivatives, i.e. biofuels, is only shortly reviewed here.

Table 1. Platform molecules: original vs. revisited.[8]

2. Catalytic production of platform chemicals from lignocelluosic biomass

As proposed by Anastas in the year 2000, the 12 principles of green chemistry provide an attractive concept to improve chemical processes.[36] Catalysis belongs to one of these principles, thus reducing the enormous amounts of waste from the use of stoichiometric reagents. Following these principles, catalysis applied to lignocellulosic biomass, represents a potential tool to selectively convert cellulose and hemicellulose-derived compounds through environmentally friendlier and more efficient processes.

Recently, the hydrolysis of polysaccharides in the presence of solid acid and bifunctional catalysts has been an area of growing interest. The use of these catalysts, as an alternative to mineral acids, gives a new approach due to its facile separation after reaction occurred, and decreases its corrosion activity and toxicity. Lignocellulosic material has to go under depolymerization and partial deoxygenation; irrespective of the desired final products, liquid fuels or value-added chemicals.

The main routes to achieve this are thermochemical and hydrolytically. There are three main routes for converting lignocellulosic biomass:

(i) thermochemical
(ii) biochemical
(iii) chemical

The thermochemical route, as its name states, consists in thermal treatment (typically via pyrolysis) of biomass to produce solid, liquid or gaseous products, which can be upgraded to synthetic biofuels. The operation temperatures vary (600-800 °C). A drawback from these primary methods is the production of intermediates that need to be first upgraded to fuels through catalytic treatments, e.g. cracking, hydro-processing and steam reforming, among others. Fundamentally, due to their nature, all types of biomass-derivates are potentially suitable to be treated thermochemically.

Contrastively, when lignocellulosic biomass is treated via the biochemical route, fungi produce enzymes that can degrade ligning, hemicellulos, and polyphenols. Nevertheless, this process is associated with slow production rates. In order to boost the production rate, the biochemical route could be combined with another pretreatment method.

Moreover, the chemical (also called chemo-catalytic) route typically employs acids either in an aqueous solution or a heterogeneous phase (including ionic liquids or solid catalysts) to catalytically hydrolyze the cellulosic biomass.[3, 37] The characteristic recalcitrance of biomass to chemical reaction and fermentation processes poses a significant challenge, which has to be overcome. When comparing the chemical nature of biomass feedstock ($C_nH_mO_o$) with conventional fossil-based feedstock (C_nH_m), its oxygen content and downstream reduction sets process limitations. Another contrasting characteristic of biomass feedstock to its fossil-based counterparts is its notable hydrophilicity, which is associated to costly multistep processing.[38, 39]

Based on this, the chemo-catalytic routes play a fundamental role in the catalytic conversion of lignocellulosic material into platform molecules, and further synthesis in the primary treatments to fuels and value-added chemicals. The chemical nature of cellulosic biomass clearly has consequences on the development of suitable catalysts. This approach displays the optimal route to selectively deconstruct the components found in lignocellulose to obtain suitable platform molecules for further desired synthesis. Recently, many solid catalyst systems have been developed for a high performance conversion of bio-based raw material into high value-added chemicals and fuels. These catalysts can be

Original platform molecules[9]		Revisited platform molecules[7]	
Succinic, fumaric and malic acids	2,5-Furandicarboxylic acid	Ethanol	Sugars (sorbitol, xylitol)
3-Hydroxypropanoic acid	Aspartic acid	Furans (furfural, HMF and 2,5-furandicarboxylic acid)	Glycerol and derivatives
Glucaric acid	Glutamic acid		3-Hydroxypropanoic acid
Itaconic acid	Levulinic acid	Bio-hydrocarbons	
		Organic acids (lactic acid, succinic acid and	
3- Hydroxybutyrolactone	Glycerol		
Sugars (sorbitol, xylitol/arabinitol)		levulinic acid)	

segregated into four main categories according to their structure, nature and substrate activation properties in agreement with Hara et al;[40] (a) micro- and mesoporous materials, (b) metal oxides, (c) supported metal catalysts, and (d) sulfonated polymers.

2.1. Ethanol

The highlighted utilization of edible biomass-derived aqueous sugars produces biofuels via fermentation into ethanol (90% of

the world biofuel production). Ethanol is the best known platform molecule due to its enormous potential. This building block can be added to gasoline, which allows the fuel to combust completely in a more efficient manner.[41, 42] The ethanol obtained this way, consumes inexpensive feedstock and results in a net CO_2 reduction. Currently, bioethanol is mainly produced from starch-based material (grain or sugarcane).[41]

The conversion of lignocellulosic biomass into ethanol follows three typical steps:[43]

(i) Pretreatment of lignocellulosic material. Mood et al.[44] published a review on the advantages and disadvantages of various pretreatment methods. This first step is characterized by the decomposition and separation of the biomass-based matter to obtain fermentable sugars. In the field of agricultural waste, steam explosion has been identified as one of the most appropriate methods.[45] The Nordic oil company St1 includes steam explosion in their production plant in Finland to produce bioethanol from sawdust.[46]

(ii) Hydrolysis of the polysaccharides to form fermentable sugars i.e. hexoses (C_6) and pentoses (C_5) is an essential step to form bioethanol. Enzymatic hydrolysis has various advantages over acid hydrolysis, including lower energy consumption, fewer corrosion problems and mild environmental conditions. However, the acid hydrolyisis reduces ethanol production costs.[47, 48]

(iii) Fermentation of C_6 and C_5 sugars to form bioethanol (including fermentation microorganisms and fermentation process). In order to achieve the fermentation of these sugars, *Saccharomyces cerevisiae* is the most typically used microorganism at industrial level. This microorganism is capable of fermenting hexoses into bioethanol, which unfortunately skips pentoses during the fermentation process. However, some engineered microorganisms have been developed in order to ferment pentoses.[49]

A recent report published the successful production of ethanol with cellulolytic bacteria growing at temperatures >70 °C.[50] The process (called consolidated bioprocessing (CBP)) is associated with the hydrolysis of cellulose and hemicellulose via enzymes. This novel process occurs in the pretreated lignocellulosic biomass and ferments hexoses and pentoses into bioethanol. One of the advantages is that no additional (hemi)cellulolytic enzymes are needed.

Ethanol can serve as a feedstock to produce hydrogen via the catalytic steam reforming.[51, 52] This route has been regarded as an attractive feedstock due to its non-toxicity. This process is associated wth the gasification of aqueous solutions of ethanol at high temperatures (typically from 600 °C to 800 °C); high availability; high hydrogen content; and atmospheric pressure using metal oxides, mixed metal oxides, supported base metals (Ni, Co, Cu), and supported noble metals (Pd, Pt, Rh, Ru, Ir). However, it comprises several other simultaneous reactions (dehydrogenation, decomposition, dehydration, etc). In order to overcome the energy-intensive distillation of this process, aqueous-phase reforming can be implemented to produce hydrogen at lower temperatures.

Additionally, the catalyst stability (deactivation due to coke deposition) and control over formation of side products (e.g. acetaldehyde, acetone and ethylene) are negatively affected by the severe temperature conditions.

The production of biomass-based polyethylene-derived plastics is a meaningful incentive to progress the bioethanol-to-ethylene (BETE) route. Ethylene (ethene, $CH_2=CH_2$) is a good starter molecule for the further synthesis of different grades of polyethylene and other bulk and base chemicals[53]. This process avoids the dependence on petrochemical sources and offers a high quality of produced ethylene. Nonetheless, high water content is found in bioethanol that presents a known issue for its employment as a feedstock or direct fuel, due to its water-removal requirement. Four different types of catalysts have been reported to successfully dehydrate ethanol into ethylene: phosphoric acid, oxides, molecular sieves and heteropoly acid catalysts.[53] After ethylene, the second go-to starting product in the current petrochemical industry is propylene, which can also be synthesized from bioethanol. Propylene can be used as a raw material to synthesize valuable chemical commodities such as polypropylene, polyacrylonitrile and acrylic acid.[54] The process to yield propylene firstly involves dehydration to ethylene, before going through the oligomerization-cracking route.[55] Zeolites usually are employed for this reaction. Recently, Xue et al.[54] employed the composite of In_2O_3 and zeolite beta to yield propylene (50%) from bioethanol.

Another important chemical is butadiene, which is formed by the transformation of bioethanol. Butadiene is another promising platform chemical, which is mainly used as a monomer in polymerization[56] and in the synthetic rubber industry, hence the manufacture of vehicle tires.[57]

The cost-effective production of straight-chain olefin value-added chemicals (e.g. ethylene, butadiene, propylene) converts bioethanol, in an exciting binding platform between biorefineries and state-of-the-art fossil fuel-based industry, facilitating a more natural evolution into sustainable energy systems.

2.1.1 Economic aspects

Ethanol is a well established biobased fuel in a fast-growing industry. Among other factors that allowed this to occur there is the well-known renewable source aspect, it is less toxic than other alcoholic fuels and it has a fractional compatibility with the existing infrastructure for gasoline. There is a current boom in the annual production of bioethanol from 50 billion L in 2007 to 118 billion L in 2016.[58, 59] Additionally, the International Energy Agency (IEA) projected that a rapid deployment of bioethanol will occur by 2020 and production costs of bioethanol would stabilize to reach around € 0.49-0.57/lge (liter gasoline equivalent).[43, 60] Thus, ethanol would become competitive at approximately 60 EUR per barrel by 2050.

Dumesic and colleagues produced bioethanol by fermentation of lignocellulosic biomass.[61] The proposed process consists of a first step where a chemical hydrolysis of hemicellulose and cellulose into soluble sugars takes place using γ-valerolactone (GVL), afterwards the fermentative sugars are upgraded into ethanol. This approach leads to high ethanol yields (>87%) and highly efficient use of the energy content of cellulose and hemicellulose. The integrated system, using agricultural waste as a feedstock, calculates a total cost of production of € 4.4 per gallon of gasoline equivalent that hints at a competitive alternative to current biofuel production systems.

In a recent scientific paper, Chen and Fu investigated the economic feasibility of an integrated industrial project in China with a bioethanol production of 20,000 t per year.[62] The project integrates various technologies such as steam explosion technology, enzymatic hydrolysis, pre-hydrolysis, saccharification and co-fermentation (PHSSCF) to produce ethanol, compressed natural gas (CNG) and lignin plastic composite material (LPCM) simultaneously. The ethanol, LPCM and CNG total production costs are 709, 135 and 32 EUR/t, respectively. On a parallel case, if ethanol were the single product the total production cost would be 878 EUR/t. Even though bioethanol production costs currently seem higher than those of fossil fuels, the feedstock costs are governed by materials and investment costs, whereas utility and variable operating costs (water, steam and, wastewater treatment) play a minor role.

2.2 Furans (furfural, HMF, FDCA)

Nowadays, the acid catalyzed hydrolysis of pentoses and hexoses has increased in importance. The conversion of these sugars affords two highly interesting value-added chemicals: furfural (FUR) and 5-hydroxymethylfurfural (HMF). HMF can be completely or partially oxidized to 2,5-furandicarboxylic acid (FDCA).

Besides homogenously catalyzed production to yield furanic compounds; current research addresses challenges mainly on the development of heterogneously catalyzed systems in pursuance of reutilization and ease to separate solid catalysts from the reaction medium; avoid corrosive and toxic effluents; and can be synthesized with broad surface acidities and porosity properties to improve selectivities. On a parallel pathway, the development and application of ionic liquids (IL, molten salts with melting points lower than 100 °C composed of large organic cations) onto these systems offers new advantageous perspectives. However, due to economic feasibility limitations, IL are not included in the present review.

The direct use of furans such as FUR and HMF are considered excellent platform molecules and often called "sleeping giants" due to various potential applications, such as:

(i)   promising additives in liquid fuels (especially 2-methylfuran and 2,5-dimethylfuran),

(ii) monomers for various polymers (such as 2,5-hydroxymethylfuran, 2,5-carboxyfuran)

(iii) chemicals for value-added products

The main advantage of the latter potential application is that a shorter process takes place, including intensified reaction conditions, to form these value-added chemicals. This route also requires less H_2 consumption, hence CO_2 emissions remain low which leads to a high carbon efficiency.

Moreover, FUR and HMF have not yet been involved directly as fuel components due to their chemical properties, such as melting points (-37 °C and 30 °C, respectively) and stability; nevertheless, they are attractive platform molecules for further synthesis into a variety of value-added furan derivatives.[63-66] Figure 1 shows the chemical pathway to form furan-based molecules using pentoses and hexoses as raw material.
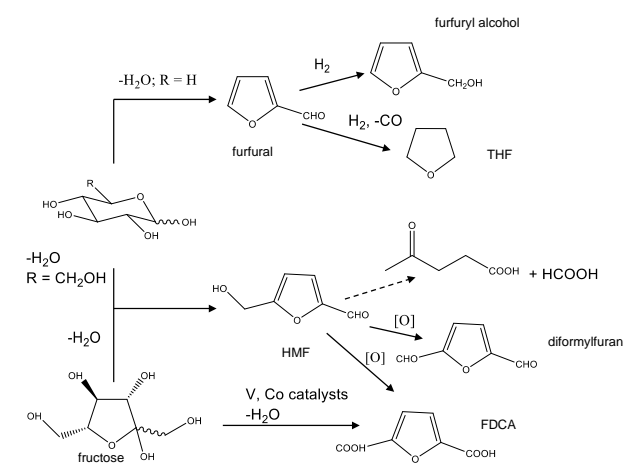
Figure 1. Synthesis and transformation of furans. Reproduced with permission from Ref. [7]. Copyright: 2010 The Royal Society of Chemistry.

2.2.1 Furfural

Furfural (OC_4H_3CHO, 2-formylfuran, furan-2-carbaldehyde, FUR), is the dehydration product of C_5-carbohydrates (i.e. xylose, arabinose found typically in hemicellulose).[67, 68] Lignocellulosic biomass is uniquely suited for FUR production. More than 80 chemicals have been identified as direct or indirect derivatives of

this building block coming from hemicellulose-rich feedstocks (i.e. bagasse, corncobs and stalks, switchgrass and hardwood).[69]

Currently, FUR is produced industrially, associated with a variety of environmental concerns, for instance toxic effluents originating from sulfuric or hydrochloric acid at temperatures <200 °C. Another issue is the high energy consumption related to the steam stripping process to avoid further FUR degradation and fuel employment to generate the steam. Besides mineral acids, organic acids have been shown to provide catalytic properties in FUR formation.[70-72] In fact, studies have shown that some organic acids are formed as secondary products from xylose dehydration as fragmentation products, i.e. acetic and formic acid.[73, 74]

New methodologies have been established considering co-catalysts of different salts in the acid-catalyzed system. This development has been emphasized in previous literature aimed at increasing the formation of FUR.[75, 76] An attractive opportunity to benefit from salts contained in seawater is to use it as an inexpensive co-catalyst in the reaction medium. A compelling example is the inclusion of seawater in biorefineries installed near the sea.[77, 78] Hence non-potable water can be potentially integrated in industrial processes.[77]

In counterpart, easily-separable solid catalysts including zeolites[79-85], aluminosilicates supported with metals,[86] modified silica;[87-94] metal oxides like alumina[95] and zirconia;[95-97] heteropolyacids;[98-100] resins;[91, 101, 102] carbon-based materials, such as sulfonated graphenes[103] and coated activated carbon[73] yield FUR in a much more environmentally conscious and efficient industrial process.

The dehydration of xylose into FUR is associated with a significant challenge that promotes the formation of by-products. An efficient approach to avoid this issue is the addition of an organic co-solvent, which would continuously extract FUR from the aqueous phase into the organic phase. Therefore, FUR would be protected in the organic solvent and hence avoid losses by humin formation, and FUR yield would be improved.[104] Several publications have reported the addition of methyl isobutyl ketone (MIBK), 2-methyltetrahydrofuran (MTHF),[105] toluene,[106] cyclohexanol,[106] tetrahydrofuran (THF),[107] dimethyl sulfoxide (DMSO),[94, 98, 108] cyclopenthyl methyl ether (CPME),[109, 110] and the widely used toluene[92, 111, 112] as efficient co-solvents for the formation of FUR from xylose. IL have also been used to back up hemicellulose depolymerization.[113] Nevertheless, the high cost of IL limit their application on an industrial scale.[114]

FUR can also be used directly as a solvent. In addition, approximately 80 chemicals derived from FUR with high potential applications have been identified.[115] The most important market of FUR is used to synthesize furfuryl alcohol (reduction at 120 °C at atmospheric pressure),[116] which represents approximately 60% of the FUR market. Furfuryl alcohol has application in the manufacture of foundry resins, component production of P-series fuels, liquid alkanes and in the food industry.[104, 117, 118] THF and tetrahydrofurfuryl alcohol are two very appealing chemicals also formed from FUR that have wide applications in the chemical industry. The rest of the FUR market is mainly divided between the petrochemical, plastics and agrochemical industries and in pharmaceutical production.[116]

FUR can also derive into levulinic acid (4-oxopentanoic acid), a promising value-added chemical from biomass, which will be discussed later. One of the many routes to produce levulinic acid via furanic compounds is the hydrolysis of furfuryl alcohol into levulinic acid.[119]

Other interesting compounds are 2-methylfuran (MF), dimethylfuran (DMF) and MTHF, which are formed via hydrogenation and can be used as biofuels.[120, 121] MF is typically employed continuously in the production of pesticides, perfume intermediates and pharmaceuticals. At present, MF is formed as a by-product in the formation of furfuryl alcohol from FUR. Even though MTHF has a lower octane number (87) than ethanol (108.6), MTHF shows more fitting biofuel aspects due to its hydrophobicity, it has a higher density and a higher heating value.[122] Therefore it is employed with ethanol and gas to create

an alternative fuel that can be used as a substitute for gasoline (P-Series Fuel). Furthermore, MTHF is a promising substitute for dichloromethane (DCM), a common solvent used in pharmaceutical and agricultural products and a probable carcinogen.[123]

Carboxylic acids can also be produced via oxidation from FUR. Furoic acid (employed in the pharmaceutical, agrochemical and cosmetic fields)[124] and maleic acid (an important raw material employed in the manufacture of textiles, food additives, plasticizers, bulk-drugs and agricultural chemicals)[125] can be formed from FUR adding O_2 as an oxidant.

2.2.1.1 Economic aspects

Although xylan and xylose could be further synthesized into profitable chemicals from the paper industry, an important quantity of the hemicellulose-derivatives are burned to provide process heat.[126] Therefore, valorization of these compounds requires a new economic approach for new ideas and new markets.

FUR has an estimated global production of 400 kt per year worldwide. China is leading the production of FUR from corncobs, accounting for 70% of the FUR in the global market. The Dominican Republic and South Africa are the other two countries producing FUR from bagasse. In contrast, FUR commercialization in Europe has been limited and penalized with antidumping taxes.[127] By 2002, the market price of FUR was around 1500 €/t.[128] This value recently sunk to 1200 – 1300 €/t[129], which is highly dependent on oil prices.

2.2.2 Hydroxymethylfurfural (HMF)

Hydoxymehtylfurfural (HMF) can be catalyticaly produced from biomass-derived hexose polysaccharides. It can also be formed from cellulose, starches and most typically from hemicellulose-rich sugars (glucose).[121] HMF formation from cellulose and starch implies the sequential process from glucan hydrolyzation to glucoses, isomerization to fructose and dehydration into HMF. This system resembles the formation process of FUR where the sugar used as feedstock goes under dehydration, losing three molecules of water in order to form the furan-based compound. This process is typically undertaken in homogenous catalysis employing mineral acids (*e.g.* HCl, H_3PO_4 or H_2SO_4), in heterogeneous catalysis using salts as co-catalysts and solid acid catalysts based on different methodologies such as polymeric resins and zeolites.[130] In order to obtain HMF from fructose, Brønsted or Lewis acids can be used as catalysts[121]. Naturally, the earliest work on HMF formation used catalysts including mineral acids. Being Wolfrom et al.,[131] one of the leading researchers on this field, used HCl in the homogeneously catalysed system to form HMF from glucose. Nevertheless, the use of homogenous acids has various evident inconveniences, especially in the separation and recovery of the liquid acid from the reaction medium, the corrosion of the equipment and the potential environmental risks.

One of the earliest methods using solid catalysts for HMF manufacture was done by Garber and Jones. They used aluminium salts as catalysts in their 1963 patent,[132] where they reported 50 mo% yield of HMF when using glucose and fructose at 240 °C and 271 °C, respectively. Dehydration of glucose into HMF faces more challenges than dehydration of fructose due to the direct dehydration path from fructose to HMF. Glucose, on the other hand, firstly requires to be isomerized to fructose. However the wider availability of glucose motivates researchers to develop new methodologies to use this candidate as HMF feedstock, even though yields are typically low for this feedstock. Hence, current research focuses on employing catalysts that isomerize glucose to fructose.[133]

However, the principal drawback in the acid conversion of C_6 to HMF (similarly of C_5 to FUR) is the serious number of undesired side reactions and the formation of insoluble polymers (humins).

This challenge is originated by the higher activation energy to form HMF than the activation energy of side product formation. Furthermore, due to the chemical nature of HMF (polarity and high hydrophobicity), it faces costly separtation operations from the aqueous phase where it is typically produced.[134]

In a paper published by J. Dumesic's research group, it was reported that it was possible to convert high amounts of fructose (90%) with high HMF selectivities (80%) in a biphasic system employing DMSO and phase modifiers.[135] Furthermore, they added an organic phase consisting of methyl isobutyl ketone (MIBK) and 2-butanol to extract formed FUR from the aqueous phase. They also reported meaningful HMF yields above 70%. Furthermore, other research groups have developed several combination systems of solvent and solid acid catalysts in this field, such as solid heteropolyacid salt $Ag_3PW_{12}O_{40}$,[133] tetraethyl ammonium chloride (TEAC)–$NaHSO_4/H_2O$,[136] phosphorous pentoxide (P_2O_5),[137] $FeCl_3$-tetraethyl ammonium bromide,[138] and sulfated zirconia/IL.[139] Nevertheless, downstream processing is still a challenging issue. Recent breakthroughs in the field point towards the addition of more selective IL in the reaction media, which includes acids or metal chlorides as catalysts.[140]

Another recent progress from Dumesic's research group is the development of a selective solid catalyst to form HMF from fructose: a polar aprotic polymer, poly(vinylpyrrolidone) (PVP), was intercalated into different silica-based catalysts. They achieved high HMF yields above 85% when using propylsulfonic acid-functionalized silica (PVP-pSO$_3$H-SBA-15 and PVP-pSO$_3$H-MCM-41) and fructose conversions above 50%.[141] Another promising material, sulfonated nanoporous polytriphenylamin (SPPTPA-1) achieved a 96% HMF yield due to its high acidity.[142] Other promising materials in the production of HMF are metal-organic frameworks (MOF), porous organic polymers (POP) and covalent organic framework (COF), which offer good chemical stabilities and flexibility for functionalization.[143]
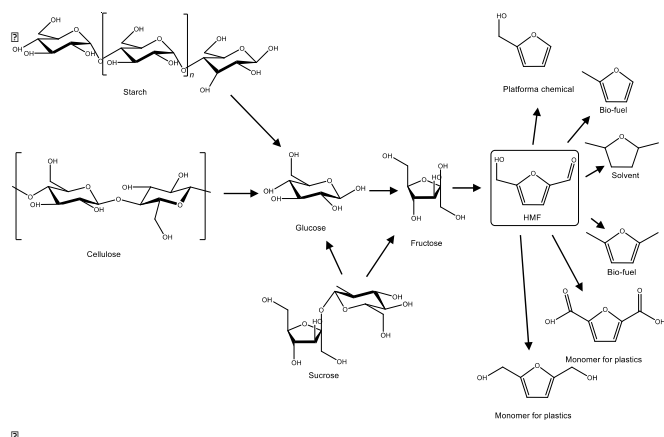
Figure 2. The synthesis of HMF from carbohydrates and its further derivatization to important chemicals. Adapted and reproduced with permission from Ref. [144]. Copyright: 2011 John Wiley and Sons.

The flexible chemistry from HMF offers many possibilities and markets, due to its reactive structure comprising a furan ring, an aldehyde group and a hydroxyl group. Four main reaction paths to synthesize further chemicals from HMF have been identified: oxidation, reduction, redox and decarbonylation reactions. HMF, together with levulinic acid are the most interesting bio-chemicals formed from cellulose. Presently, HMF is employed as raw material to synthesize diformylfuran (DFF) and FDCA via oxidation. DFF is an attractive raw material for the production of

pharmaceuticals, fungicides, furanic polymers, etc.[145] 2,5-dimethylfuran (DMF), a high caloric biofuel derivative, is produced via reduction reaction. In addition, many other valuable products have been identified via reduction such as furfurylalcohol, 2,5-dihydroxymethyltetrahydrofuran, 5-methyltetrahydrofurfuryl alcohol, 2,5-dimethyltetrahydrofuran and furan-2,5-dimethanol (FDM). FDM can also be converted with 80% of yield using NaOH as reported previously via redox reaction.[146] Another important compound formed via redox reaction is alcomxymethyl furanoic acid, which can be employed as a surfactant.[145, 147] Additionally, HMF could find use in the biofuel (as ethoxymethylfurfural, dimethylfuran, 2-Methylfuran) and pharmaceutical markets (as 2,5-Diformylfuran, 2,5-Furandicarboxylic acid), in a similar way to that of ethanol. Furthermore, not only can a new generation of biofuels be formed from HMF, but also a broad range of intermediates and fine chemicals can be synthesized from it. For instance, another interesting route is the formation of levulinic acid and formic acid from HMF, both acids can be further transformed into biofuels and chemicals.

Nonetheless, numerous challenges exist with the HMF chemical properties that make it unattractive as a liquid fuel, i.e. instability in a non-neutral solvent system, low energy-density and high reactivity. An interesting platform molecule, 5-(chloromethyl)furfural, has been suggested as a functional substitute of HMF with a more practical approch for its production process.[148, 149]

According to recently published literature heterogeneous approaches developed for HMF production deploy decreased optimum temperatures (hence decreasing humin formation and boosting HMF yields).[143]

2.2.2.1 Economic aspects

A recent techno-economic study evaluated a DMF and HMF biorefinery facility, employing fructose as a raw material.[150] DMF is obtained from HMF with the addition of a Cu-Ru/C catalyst. The process follows a 300 metric ton/day of fructose feed rate and the fixed cost of available fructose is €260 per metric ton, assuming an operational time of 20 years. The estimated total capital investment is calculated at €138 million. The minimum selling price for HMF is calculated at €0.94 per kg.

In the case of DMF, the estimated total capital investment is approximately €165 million and the minimum selling price of DMF is €1.95/kg. However, the total capital investment value is estimated for the direct transformation of fructose to DMF.

The authors also highlighted two main process disadvantages: the dependence on H_2 to convert HMF to DMF and the salt requirements to enhance extraction of HMF and downstream separation.

The price range of both HMF and DMF, of around 1 and 2 euro per kg, would be a good base to compete with other bulk chemicals originating from fossil fuel-based raw materials.

### 2.2.3 Furan-2,5-dicarboxylic acid (FDCA)

2,5-furandicarboxylic acid (FDCA) is also a very attractive biobased platform molecule because it can be employed as a substitute for terephthalic acid and polyethylene terephthalate in the production of polyesters.[151]

Even though there exist several paths to afford FDCA, the majority of reactions take place via oxidation of HMF. This reaction path faces several challenges that include the formation of condensation products even at low temperatures (373 K) and the incomplete oxidation of HMF to FDCA, which causes the production of partially oxidized undesired compounds. As is the case with many chain processes, improvements in HMF formation favor production of FDCA.

As Figure 3 shows, the formation of FDCA via HMF oxidation includes the generation of partially oxidized intermediates 2,5-diformylfuran (DFF) and 5-hydroxymethyl-2-furancarboxylic

acid (HMFCA), which in addition are oxidized to produce 5-formyl-2-furancarboxylic acid (FFCA) and finally FDCA.

Currently, research on this field focuses on the development of bimetallic catalysts with a carefully designed size and composition that have proven to be promising in improving catalyst activity. Albonetti et al.[152] synthesized titania-supported Au and Au-Cu nanoparticles, obtaining good catalytic activity and stability in the oxidation of HMF to FDCA. Lilga et al.[153] developed a system with HMF in an aqueous solution of acetic acid with a Pt/ZrO$_2$ catalyst. The reactor operates at 10 bar and 100 °C and yields 90% FDCA. In the case of Motagamwala et al.,[154] they employed a Pt/C catalyst to yield 93% FDCA from HMF that was formed from fructose in a GVL/H$_2$O biphasic system.
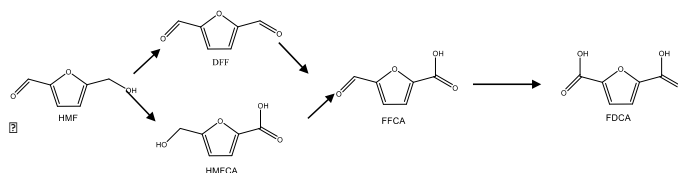
Figure 3. Reaction pathway for aqueous oxidation of HMF. Adapted and reproduced with permission from Ref. [155]. Copyright: 2015 Elsevier.

FDCA also finds wide-spread utilization as a feedstock to produce renewable plastics including bottles, food packaging and automotive applications. Currently, Avantium operates a pilot plant in the Netherlands to synthesize levulinics (methyl levulinate), alcohol (methanol) and FDCA from carbohydrates in two catalytic steps.[156] This process involves the dehydration of the bio-based sugar in an alcohol media to produce methoxymethyl furfural (MMF) instead of HMF, which would be produced in water. After MMF has been formed, it undergoes catalytic oxidation in acetic acid to yield FDCA.

2.2.3.1 Economic aspects

Triebl et al.[157] proposed two different models to produce FDCA from oxidation of HMF, where they propose a minimum selling price of €2750/t. Nevertheless, this amount would decrease if pure oxygen were to be replaced by air as oxidant in the system. They claim that with this process, the FDCA is close to 100% purity. It has been suggested, that oxidation of HMF at high concentrations could afford more economic production of FDCA.[154]

Currently Avantium is manufacturing PEF and FDCA in its plant in the Netherlands and in the preparation of the construction of the first FDCA production plant. In early 2018, Synvina (Avantium joint venture with BASF) disclosed plans to extend the pilot phase in Antwerp. This would be the first commercial-scale plant to produce FDCA.[158, 159]

2.3 Glycerol and derivatives

Glycerol is a colorless, odorless, non-toxic water-soluble viscous polyol compound. Glycerol offers a unique chemical versatility due to its C3-backbone with a corresponding number of alcohol groups. It also has a high boiling point (290 °C), which gives advantages over more volatile compounds in industrial processes. Glycerol can be obtained commonly by:[160]

  I. Hydrolysis. Water and a catalyst are commonly used to yield glycerol and fatty acids.
  II. Saponification. Basic saponification and a catalyst are employed to form glycerol from triglyceride (Figure 4).
  III. Transesterification. Biodiesel is usually produced by the transesterification reaction of vegetable oils and animal fats (Figure 5). The most common catalysts used in this chemical pathway are alkaline bases (e.g. alkaline earth metal hydroxides). The products of these

reactions include methyl ester, biodiesel, ethyl ester, and glycerol.[161]

However, these synthesis processes do not include fermentation or hydrogenolysis, because they are currently not industrially applicable.

The production amount of glycerol and biodiesel follow a volumetric ratio of 10:1 in the transesterification reaction. This versatile platform molecule is derived as the main by-product from biodiesel production, which makes it important as a renewable feedstock to increase alongside biofuels.[162] This market growth is mainly due to the rapid development and expansion of biodiesel production.
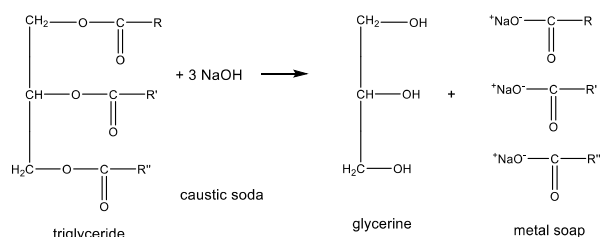
Figure 4. Basic reaction of the saponification process. Adapted and reproduced with permission from Ref. [160]. Copyright: 2013 Elsevier.

The term glycerol is often used in the literature as the pure substance, whereas the terms glycerin or glycerine are assigned to commercial solutions of glycerol in water in different concentrations. Afterwards crude glycerol is usually treated and distilled into separate chemical additives in order to produce a significant range of glycerin, typically containing more than 95% glycerol.[163]
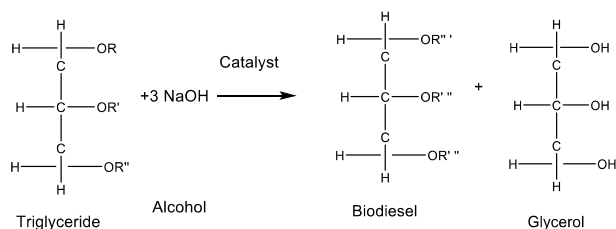
Figure 5. Stoichiometric reaction of triglycerides and alcohol. Adapted and reproduced with permission from Ref. [160]. Copyright: 2013 Elsevier.

New applications have been promoted for this building block by transforming glycerol into commodity chemicals via reduction, oxidation, dehydration, esterification, hydrogenolysis and acetalization, amongst others.[164] Glycerol has many applications in the pharmaceutical, cosmetic and food product industries. Furthermore, glycerol polymers have impressive applications in biomedicine.[165]

Quispe et al.[160] listed various applications of glycerol in their review. Similarly to ethanol (EtOH), aqueous glycerol can be converted into CO, H_2 and CO_2 via steam reforming, partial oxidation and autothermal reforming.[166-168] Glycerol can be used as a fuel additive, animal feed, food acrolein, in chemical and pharmaceutical products; and methanol, ethanol and biogas can be also produced. Miranda et al.[169] published a research on the effects of bimetallic Ni-Cu systems on the conversion of glycerol into different value-added compounds (methane, hydroxyacetone, pyruvaldehye). They concluded that the catalytic conversion of glycerol is ruled by the geometrical effect that Cu has on Ni. An interesting paper by Chimentão et al.[170] studied the sources of deactivation of glycerol when employing a Ni/γ-Al$_2$O$_3$ catalyst. They identified metallic Ni species as participants in the hydrogenolysis route of glycerol, whereas NiO sites promote its dehydration forming methane and hydroxyacetone. In a similar work, they also identified non-noble metals like cobalt as key

players for glycerol conversion into hydroxyacetone, pyruvaldehyde, lactic acid and lactide.[171] An attractive monomer, 1,3-propanediol, is increasingly being produced from glycerol since the late 1980s. An industrial production pathway was developed by DuPont and Genencor by developing a recombinant *E. coli* strain from glucose. An alternative to this pathway is to produce 1,3-propanediol from glycerol with natural microorganisms or genetically modified strains.[172] Even though some obstacles should be overcome to scale up the process to produce 1,3-propanediol from glycerol such as low productivity and high costs, microbial production from glycerol seems to be sustainable. Besides, the first steps toward industrialization has been taken in Jiangsu, China, where a facility with a capacity of 20,000 tons/a has been built.[173]

On the other hand, polyols have been widely used in the industry as feedstock to synthesize polyurethanes with different properties, hence they offer a wide range of potential applications as foams, coatings, insulation material, mattrasses and elastomers by causing a reaction with isocyanates.[174] Currently the polyol industry depends heavily on fossil-based materials. Polyols can also be synthesized from vegetable oils via epoxidation, transesterification, hydroformylation, ozonolysis and thiol-ene addition. Kennedy et al.[175] recently published a model predicting H_2 production from polyols employing Pd nanoparticles on TiO_2 at 0.5% weight.

2.3.1 Economic aspects

Glycerol production is directly related to the biodiesel production process (10% of glycerol is generated as a by-product).[176] It has over 2,000 different applications.[177] Current glycerol production is about 700 000 tonnes per year. According to Tan et al.[167] the major industrial application of glycerol is found in the manufacture of drugs and pharma (18%), followed by personal care (16%) mainly to provide lubrication, to improve smoothness and as a humectant. Glycerol can be used in the polyether (14%) and food industries (11%). The largest glycerin consumers are Western Europe, China and the United States.

The current market price for glycerol (80% purity) is between €0.08 and €0.17/kg. However, these values might change soon. The constant development of glycerol applications and the rapid expansion of the biodiesel industry, which is forecast to produce 45 billion liters by 2020,[178] could boost the glycerol market that caused the prices to decrease (from €0.47/kg in 2004 to €0.04/kg in 2006), but over the next 10 years it is expected to increase in line with inflation. Hence, the development of the biodiesel industry, that will lead to plentiful low-cost glycerol for further value-added synthesized materials and chemicals, is still to come.

2.4 Biohydrocarbons

Significant research advances have gradually appeared, unfolding new processes for the biological transformation of lignocelullosic-derived sugars into biohydrocarbons. This recent wave of opportunities comes along with recent advances in fermentation processes, which allow industry to design and develop specific microorganisms to produce various biohydrocarbons. The main goal of creating these platform molecules is to generate various fuel compounds.

The biohydrocarbons include short-chain hydrocarbons (C_5-C_{12}) long-chain alkanes (C_{10}-C_{23}) and isoprenoids (isoprene, farnesene, bisabolene and pinene)[151]. Depending on the alkane chain length, their applications vary. Short-chain alkanes are typically used as a gasoline substitute, whereas long-chain alkanes can be employed as jet fuel and diesel. Generally, the biohydrocarbons can be synthesized by two paths that include either lignocelullosic-based sugars, using genetically modified microbes, or directly using photosynthetic bacteria.

2.4.1 Isoprene

Isoprene is a very versatile platform molecule with highly reactive properties due to the C-C double bonds in its C_5 chain. It is generally employed to produce synthetic rubber. Isoprene has various other applications, for example as adhesives and elastomers. Furthermore, it can also be used as a fuel additive in gasoline, diesel and aviation fuel.[179] Isoprene is used mainly in the manufacture of polyisoprene or "synthetic" natural rubber, which is consequently used to make tires. Furthermore, isoprene can be widely used in the fields of isoprenoid medicines and fragrances.

Isoprene is currently produced from fossil fuel-based sources, generally by direct isolation from C_5 alkanes in the cracking process. However, the natural process of isoprene synthesis can take place in animals (i.e. humans), plants (which produce the largest quantity of isoprene up to 600 million t/year), yeast, and bacteria.[180]

Currently, isoprene is produced almost entirely from fossil fuel-based feedstock. There are four principal synthetic routes that have been scaled up by numerous companies (Bayer, IFP, Marathon Oil and Kuraray) to form isoprene.[181] The well-known petrochemical process (Sumitomo Chemical) to produce isoprene improved the processing route by adding CH_3OH and O_2 with H_3PO_4-MoO_3/SiO_2 and mixed oxide systems (Figure 6).
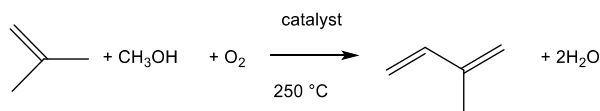
Figure 6. Improve route for the catalyzed production of isoprene. Adapted and reproduced with permission from Ref. [181]. Copyright: 2015 Elsevier.

In the bacterial process the main microorganisms used are *B. subtilis*, *E. coli*, *cyanobacteria* and *S. cerevisiae*. In the bacterial process to form isoprene, two routes have been identified, the mevalonate (MVA) pathway and the methylerythritol-phosphate (MEP) pathway. The Danisco US Inc. in collaboration with The Goodyear Tire and Rubber Company as well as Genecor (Dupont) have successfully engineered *E. coli* yielding 60 g/L via fermentation with an MVA pathway.[182] Furthermore, Ajinomoto and Bridgestone are collaborating to develop a method to produce bio-isoprene via fermentation.[183]

Morais et al.[181] performed a comparison study of the fossil fuel-based and biochemical-based isoprene production processes employing green metrics that include material and energy efficiency factors, as well as economic aspects. They calculated production prices of 4.3 k€/t and 4.9 k€/t of isoprene for fossil based and bacterial based processes respectively. A disadvantage of isoprene production with microbes is its requirement of a carbon source originating from agricultural crops, which might affect food and feed prices.

In comparison to the most famous platform molecule, ethanol, isoprene has several advantages over that alcohol. Isoprene is much easier to separate from the fermentation broth, fermenting bacteria tolerates isoprene better than ethanol and isoprene is more versatile in forming more complex chemicals through biochemical and thermochemical routes.

2.4.1.1 Economic aspects

Isoprene is a very attractive biohydrocarbon with a current world market of €0.8–1.7 billion, and it is foreseen to grow to €2.5 in 2021. Global demand amounts to around 800,000 t/year. While Russia still dominates global isoprene demand (Nizhnekamskneftekhim, Synthez-Kauchuk and Togliattikauchuk are the major producers of high-purity isoprene with a production of 427,500 tonnes in 2011),[181] future growth is potentially expected in developing economies like Asia (especially in China) and Latin America.

High prices in isoprene production are one of the main motivations in producing bio-based isoprene. The economic aspects of isoprene production are linked to naphtha and premium gasoline in a way that glycerol is linked to biodiesel production costs. These aspects also include the relationship to the overall energy costs associated with isoprene production and fossil fuels. As crude oil prices have been sinking in the last few years, feedstock costs may not be so competitive currently, but promise to improve.[184] The research of Morais et al.[181] concludes that glucose costs dominate the techno-economic view of the isoprene production process. Hence there is a continuous need to exploit C_6 sugars, making lignocellulosic biomass a great alternative. Furthermore, the biological (fermentative) pathway to produce isoprene requires less material and energy than the petrochemical isoprene production pathway. The possibility of progressing with low-cost biomass-based sugars to convert them into value-added chemicals with fewer natural resource requirements provides a green option to produce isoprene.

2.5 Organic acids (lactic acid, succinic acid and levulinic acid)

Organic acids (ranging from C_1 to C_6) serve as an important class of renewable chemicals that are also obtainable from lignocellulosic matter. These acids include a compelling fraction which is obtained by a minimum number of process steps from industrial sugar-rich streams, and are very attractive as platform chemicals.[7] In the past decade, significant developments in the valorization of biomass into organic acids have been observed including oxidation, anaerobic and aerobic systems, which represent a singular pathway to produce these types of platform molecules. In comparison to various other routes of biomass valorization, the pathways involving organic acids production tend to neglect the use of expensive reagents such as H_2.[185] Moreover, the transformation of lignocellulosic feedstock requires various enzymes and microorganisms to act in synergy, which is challenging, but presents a worthwhile opportunity to develop new routes and engineered strains to overcome these issues.

2.5.1 Lactic acid

Lactic acid (2-hydroxypropanoic acid, LA) is a consolidated bioproduct in the world market and about 70% of the LA market is used in the food industry. LA is an encouraging renewable building block for the development of biodegradable plastics and is an attractive feedstock to substitute current petrochemical-based materials (e.g. soda bottles). LA is a versatile platform molecule due to its hydroxyl group and carboxylic acid group, and its price is declining as its commercial availability increases. As a highly promising platform molecule, LA and its derivatives are extensively employed in the food and pharmaceutical industries. New applications have been recently intensified from this building block[186] in the field of commodity chemicals,[187, 188] such as propylene oxide and propanoic acid, liquid fuels[118] and polymers.[186] Among the polymers, one breakthrough has increased interest from several major corporations to synthesize biodegradable polylactic acid (PLA), which is biobased and compostable. PLA synthesis includes polycondensation of LA monomers and the removal of by-products (water and alcohol) from the reaction medium.[189]

LA is typically obtained via carbohydrate fermentation from C_6 sugars (glucose and fructose) after pretreatment with acids or bases (about 90% of all LA produced worldwide, which accounts for approximately 130 000 – 150 000 t), but it is also possible to synthesize LA via chemical routes. The biochemical pathway usually takes 2-4 days and exhausts a significant amount of calcium hydroxide that is used to balance the pH value of the reaction medium, hence producing a large amount of waste.

However, this route faces two main cost related drawbacks that are associated with sugars used as feedstock and sterilization.[RW.ERROR - Unable to find reference:623] Nevertheless, lignocellulosic biomass is forecast to decrease in cost and it holds potential to replace conventional feedstocks to produce LA.[190] Aside from the costs associated with the production of LA, the development of high-performance LA-forming microorganisms is a significant issue to be considered in developing strong long-standing LA biorefineries. Furthermore, an essential factor in developing strong LA biorefineries is related to the location of the site and to achieve sustainability over their fossil fuel-based counterparts.[191] The chemical route faces several constraints due to the use of hydrogen cyanide (HCN) that forms lactonitrile and acetaldehyde, which are associated with environmental concerns.[192]

It is possible to substitute the use of toxic chemicals with solid catalysts in order to convert carbohydrates to LA or lactates.[193] Chambon et al.[194] reported a direct way to form LA from cellulose over tungstated alumina and tungstated zirconia resulting in yields of 27% and 18% respectively. Nevertheless, the high concentration of sodium hydroxide makes it laborious to separate from sodium lactate. Likewise, Holm et al.[195] employed Lewis acidic zeotype materials to convert mono- and disaccharides into methyl lactate, such as Sn-Beta. They employed a methanol solution with sucrose as the substrate at 160 °C to reach a 68% yield of methyl lactate. Nevertheless, when using water as a solvent, it led to the formation of less than half of LA (<30%).[195] Yang et al.[126] achieved the transformation of xylose and xylan into LA employing a bifunctional zirconia (with yields of 42% and 30%, respectively). They conclude that the acid/base pairs on the zirconia surface aids the retro-aldol condensation of xylose, which promotes the transformation of xylose into LA. The bifunctional zirconia also promotes the conversion of xylose derived C_3 aldehydes into LA.[126] Besides the solid catalysts above mentioned, other solid base catalysts, including hydrotalcites,[196] magnesium oxide,[197] and supported noble metal catalysts[198] can be employed to produce LA from biomass feedstock.

2.5.1.1 Economic aspects

LA has market demand in sectors that theoretically have very large-volume uses such as personal and home care, biodegradable plastics, food and beverages, pharmaceuticals and animal health.

Recently, Alves de Oliveira et al.[RW.ERROR - Unable to find reference:623] reviewed the economic and production outlooks for LA. From a global perspective, production of LA has been on a steady increase since the early 1990's and will contnue to rise further as new applications and commercial ventures develop. The demand for LA has been estimated to expand by 16.9% from 2015 to 2022. The worldwide amount of LA produced industrially in 2016 was 1220 kt.[199, 200] Additionally, it is forecast that demand of LA will reach 1960 kt in 2025.[RW.ERROR - Unable to find reference:623] According to the cost analysis performed by Datta et al.,[190, 201] the base manufacturing cost of LA is approximately 0.48 €/kg. Depending on the final application of LA extending from food to feed grade (97% purity) to the higher pharmaceutical grade (98% purity).[202] However, the final price can currently vary from €2.6 to €3.4/kg and it fluctuates usually with the price of fermentation feedstock such as commodity starch and sugar.[190, 203]

Among various companies dedicated to LA production three main manufacturers are leading the global market on LA production: Corbion-Purac in the Netherlands (supplying from food, chemicals and plastics to biomedicine and beyond),[204] Galactic in Belgium (leading the development of sustainable LA production for food, feed, personal, healthcare and industrial markets)[202] and the giant chemical producer Cargill (NatureWorks LLC) in the USA.[205] NatureWorks LLC was the pioneer in building the world's first full-scale PLA plant, which was designed to produce 140 000 t annually. Should the prices of LA continue to drop, commodity chemicals from LA could become competitive with those originating from a petrochemical basis in the near future.

2.5.2 Succinic acid

Succinic acid (1,4-dicarboxylic acid, butanedioic acid, SA), a four-carbon dicarboxylic acid is drawing considerable attention for its versatile chemistry due to its two carboxylic groups. SA is a colorless crystal, soluble in water, and one of the strategic building blocks that can be transformed into a diverse range of valuable chemicals. SA can be utilized for the production of detergents, surfactants, additives, pigments, resins, foaming agents, ion-chelator in the metal industry, biodegradable solvents, food, and pharmaceutical products.[206] SA is normally produced by plants, animals (including humans) and microorganisms; among these living organisms aerobic and anaerobic microbes present promising results in the formation of SA.[7] Among these microorganisms, together with the well-studied *E. coli*[207] and the current available genetic tools, high yields of SA are attainable. Genetically engineered microorganism strains can bring high yields of SA. SA has been successfully produced from various biomass sources, such as wheat, corn waste, rapeseed, rice straw, bagasse and others.[208] As a means to improve the competitiveness of the biological production of SA, present and future challenges have to be overcome including boosting succinate concentrations and yields via metabolic engineering; overcoming the substrate repression effect; and including low-cost non-edible feedstocks to integrate biomass-based processes. SA can also be synthesized via chemical routes including paraffin oxidation, catalytic hydrogenation or electroreduction of maleic acid or anhydride.[209, 210] However, current research has focused especially on the fermentative process of SA synthesis.

Once SA is formed, it can be feasibly subjected to esterification, amidation and hydrogenation in aqueous media. Clark et al.[211, 212] published the successful transformation using Starbon® in the esterification reaction of SA in aqueous phase.[212] SA hydrogenation can also be promoted by supported noble metals (e.g. Pd,Ru) for the selective production of γ–butyrolactone (GBL). SA can also be readily converted to other bulk chemicals like 1,4-butanediol, GBL or THF.[213]

2.5.2.1 Economic aspects

The industrial potential of SA was acknowledged in the 80s for the first time. In 2015, the world market volume of SA was reported to be 59 kt/year and it is projected to have a growth rate of 27% between 2016 and 2021 each year.[214] The selling price range ranges from €2050 – 2550 per ton.[213]

Amongst the several SA manufacturers across the globe, such as BioAmber (Canada), Succinity (Germany), Nippon Shokubai (Japan) and Linyi Lixing Chemical Co., Ltd. (China); the biggest plant known until today, that produces SA from biomass, is Myriant (USA),[215, 216] which is located in Louisiana and produces up to 77 kt/year of SA from maleic anhydride.

An interesting perspective on this field was reported by Efe et al.[217] who developed a techno-economical approach for a plant producing SA with aerobic fermentation employing *S. cerevisiae* and ZSM-5 zeolite to adsorb SA. The lowest total capital investment required for the scenario is €125 million for a plant capacity of 30 kt/year.

2.5.3 Levulinic acid

Levulinic acid (also named 4-oxopentanoic acid, LVA) is a highly promising chemical intermediate that can be converted to a variety of valuable chemicals. LVA is a valuable platform chemical demonstrating carboxyl and carbonyl functionalities that give a high grade of chemical versatility.[218] This gives LVA advantages over other chemicals, since its versatile structure allows it to react both as a carboxylic acid and as a ketone.

As a promising platform molecule, LVA is a starting material of various industrial applications, such as fine organic synthesis, animal feed and food as well as polymer materials, plasticizers, extenders for fuels, herbicides, solvents and coatings.[219-221]

LVA synthesis is achieved via dehydration of hexoses using an acid catalyst (usually H_2SO_4). Once HMF is produced, it can be further decomposed into LVA (Figure 7). One of the earliest works on LVA production is from Thomas and Schuette, who used HCl as the acid catalyst with sucrose, dextrose, levulose and starch in 1931.[222] Usually, to form LVA from sugars, higher acid strengths and longer residence times are required than to form HMF. The main drawback of using mineral acids is the separation phase from the reaction medium. Its separation negatively affects downstream processes (such as GVL production). Thus, LVA can be obtained with a maximum theoretical yield of 72% from a hexose implementing base in the Biofine process due to its efficient reactor system and polymerization inhibitors.[223, 224] Furthermore, the Biofine process enables the use of low-cost and wide ranging lignocellulosic wastes including paper mill sludge, urban waste paper, and agricultural residues. Pileidis and Titirici[225] collected the reported yield of previous results, 81% being the highest when fructose is used as a feedstock and 3.6-7.2% when HCl is employed as a catalyst.
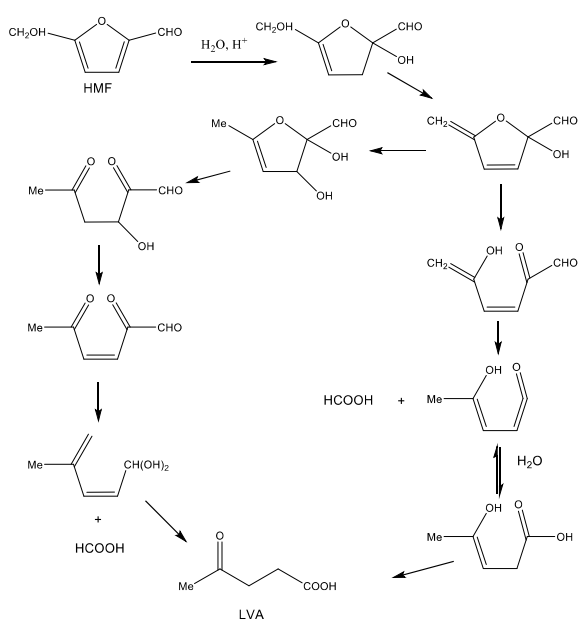
Figure 7. Conversion of HMF to LVA. Adapted and reproduced with permission from Ref. [121]. Copyright: 2015 Elsevier.

Researchers have also tried to replace homogeneously catalyzed systems with heterogeneously catalyzed systems with promising results when using glucose and fructose in aqueous solutions.[226] Another pathway to form LVA could be from acid treatment (using mineral acids or solid acid catalysts) of hemicellulose-derived C_5 sugars through dehydration into FUR and a further reduction to furfuryl alcohol.

As a versatile platform molecule, LVA can be converted into fuels by a number of catalytic routes combined with thermal deoxygenation reaction.[227] The catalytic hydrogenation of LVA leads to GVL. GVL is a value-added chemical and starting material to synthesize a broad scope of valuable chemicals such as pentenoic and pentanoic acids, fuel additives, polymers and a stable organic solvent for biomass-based processes including MTHF formation.[122, 228, 229] GVL is non-toxic and is stable at normal conditions in water and in the presence of air,[230] which makes it an attractive biofuel component.[231, 232]

In this regard, the use of solid catalysts has been widely investigated in both gas and liquid phases. Wright and Palkovits[233] recently published a review on various routes to form GVL from LVA using mostly solid acid catalysts. Hence, the present review highlights the most recent and relevant methods for it. GVL can be directly synthesized with almost quantitative

yields through selective reduction of commercial or biomass-derived LVA at low temperatures (<200 °C) utilizing non-acidic catalysts (*e.g.* Ru/C).[234, 235] Tang et al.[235] recently published a review including the production of GVL when using various external hydrogen sources, such as H_2, formic acid and alcohols. They suggest that the management of liquid alcohols is more convenient than molecular H_2. Besides, the catalytic transfer hydrogenation is more economically feasible due to the use of less expensive base metal catalysts. In the MTHF formation process, non-noble metals are generally more readily available to synthesize MTHF from LVA, due to their inexpensive nature compared to noble metals. Recently, a promising route has been developed by Dumesic and coworkers,[236, 237] avoiding the employment of noble metal catalysts and external hydrogen.[237]
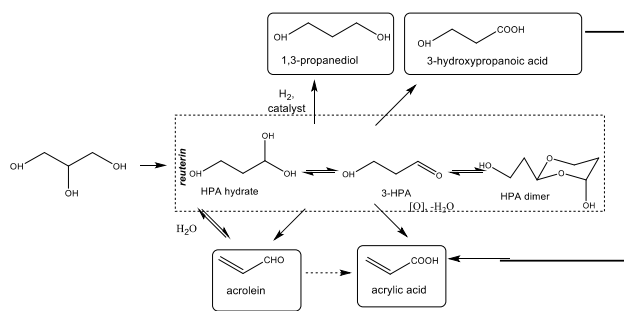
2.5.3.1 Economic aspects

LVA and its derivatives have applications in a high variety of industries, although it possesses a status as an expensive and niche specialty chemical (about 500 t/year at €7.5-€11.3/kg).[229] Mostly, current commercial plants that produce LVA have developed their process based on Biofine technology transforming diverse biomass material into various value-added chemicals. Founded in 2008, GF Biochemicals is the only operating industrial plant producing LVA from cellulosic feedstock. They produce approximately 10 000 MT/year of LVA[238] and intend to scale it up this year. However, there are other pilot plants in the USA and in Europe with smaller capacities. These new developments could motivate different industries to embark on new production plants for LVA, employing lignocellulosic biomass.[239]

2.5.4 3-Hydroxypropanoic acid/aldehyde

Chemically, 3-hydroxypropanoic acid (β-lactic acid, 3-HPA) is a three-carbon compound with strong versatility for organic synthesis due to its carboxyl and hydroxyl group.

Current production of 3-HPA is associated with various organo-chemical processes from different feedstocks, such as acrylic acid, 3-propiolactone, CO_2, glycerol and 1,3-propanediol (Figure 8); two promising routes can be identified: one from glucose and the other from glycerol. Both pathways have been reported to produce up to approximately 50 g/L 3-HPA.[240] Interesting reviews on the current status of 3-HPA biological and biochemical production have been published recently where the challenges, including its toxicity and the vast range of synthesis routes, have been addressed.[241, 242] Among various alternatives on the 3-HPA synthesis pathways, different strains have been employed to yield important amounts of 3-HPA, among these there are *Acetobacter sp.*, *E. coli*, *K. pneumoniae*, *S. cerevisiae.* Recently, interesting biosynthetic routes to form 3-HPA have been developed by Cargill Inc and other organic compounds.[243]

The potential applications of this chemical building block are enormous. It can be utilized as a monomer for (co)-polymerization, as a starting material for the synthesis of other commercially useful chemicals, such as 1,3-propanediol (PDO), methyl acrylate, acrylic acid, propiolacton and acrylamide. Moreover, the self-condensating repeating unit of 3-HPA forms a polymer, poly (3-hydroxypropionic acid), which shows promising properties as a potential substitute of traditional petroleum-based polymers due to its enzymatical and hydrolytical degradablity, its excellent glass transition temperature (-20 °C), very good mechanical properties and high melting point (77 °C).[244]

Figure 8. Production of 3-HPA and relative derivates. Reproduced with permission from Ref. [7]. Copyright: 2010 The Royal Society of Chemistry.

2.5.4.1 Economic aspects

The biggest producers worldwide of 3-HPA are Cargill Inc., Lion Apparel Inc., BASF SE and Novozymes. Although many chemical and biochemical processes have been researched on and suggested as promising pathways for the production of 3-HPA, none is commercially feasible on an industrial scale due to low yields and high production costs, especially costs related to the starting materials and operation. Nevertheless, BASF, Cargill Inc. and Novozymes successfully synthesized 3-HPA on a pilot scale level in 2013. Additionally, Cargill Inc. and the USDOE have plans to invest over €5.1 million to synthesize 3-HPA from renewable resources.[245]

On this subject, a chain process to separate and purify 3-HPA in an efficient and cost-effective downstream process will be of significant value.

2.6 Sugar alcohols (sorbitol and xylitol)

Sugar alcohols, also called polyalcohols, are obtained when the carbonyl groups of carbohydrates are hydrogenated to hydroxyl groups under high pressure and temperature (4-12 Mpa and 403-423 K). Sugar alcohols are non-cariogenic, they add sweetness with low-calorie properties and add a cooling effect to their wide range of industrial applications.[63] They have applications in the food and pharmaceutical fields, besides their characteristical platform molecule characteristic ability to be employed as feedstock for synthesizing several value-added chemicals. The most interesting sugar alcohols emerging from biomass production processes are sorbitol, erythritol, mannitol and xylitol. Xylitol and sorbitol are commonly used in pharma and food companies, personal care products and as a precursor for value-added derivatives.

Alditol sugars such as sorbitol, xylitol, and mannitol can be synthesized via catalytic hydrogenation of the corresponding aldoses or ketoses (sorbose, xylose, mannose, etc.) employing solid catalysts, e.g. niquel catalysts. An alternative is through biochemical pathways using *E. coli* as an effective host organism.
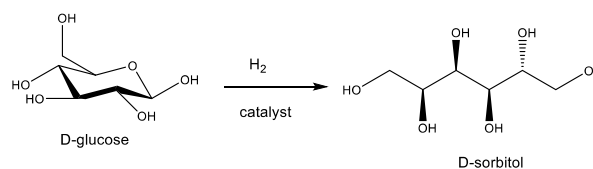
2.6.1 Sorbitol

Sorbitol is a six-carbon sugar alcohol with six hydroxyl groups. It shows high solubility in water and low sweetness. Its chemical structure gives sorbitol a high versatility for a various range of applications in the food and chemical industries. The pharmaceutical, cosmetic and textile industries utilize it as drug delivery system and humectant. Sorbitol can be further synthesized into other value-added chemicals, such as sorbitan, glycol, glycerol, and LA. It can also be converted to light alkanes via aqueous phase reforming with Pt/Al_2O_3 catalyst as Huber and Dumesic reported.[246]

Various pathways exist to produce sorbitol. In the past, it has been extensively reported about the utilization of *Z. mobilis* as an effective fermenting organism from fructose or glucose to yield sorbitol via glucose-fructose oxidoreductase.[247] Sorbitol, together with mannitol, can also be selectively yielded via hydrolytic hydrogenation of cellulose, as Matveeva et al.[248] reported using polymeric catalysts in subcritical water. Recently, Park et al.[249] published a review with engineered microorganisms (*i.e. L. plantarum*, *L. casei*) to produce sorbitol from glucose and lactose. De Boeck et al.[250] developed a strategy to avoid the uptake and reutilization of sorbitol when producing sorbitol from lactose. Moreover, they demonstrated the potential of a strain (BL300) that synthesizes sorbitol from whey permeate, which adds value to waste from the dairy industry.

Sorbitol can also be obtained through catalytic conversion of several polysaccharides (especially starch) via hydrogenolysis typically on Ni (Figure 9). Recent work has reported high conversions of glucose (95%) to yield 84wt% sorbitol using a mesoporous Ni/NiO catalyst[251], which is associated with the acid side density of the catalyst, its high surface area and high acid site availability with low deactivation degree in reusability tests.

Moreover, Ru has also shown catalytic activity to produce both sorbitol and mannitol from monosaccharides.[251] Ru can also convert cellulose directly into sugar alcohols. Sousa Ribeiro et al.[252] reported high cellulose conversion of cellulose (75%) in 5 h to sorbitol. Tronci and Pittau reported 100% glucose conversion employing Ru/C with a 23% selectivity into Sorbitol at 200 °C in 2 h.[253] The authors claim higher glucose conversion when using Pt in comparison to Ru.

Figure 9. Catalytic hydrogenation of D-glucose into D-sorbitol. Adapted and reproduced with permission from Ref.[254]. Copyright: 2003 John Wiley and Sons.

2.6.1.1 Economic aspects

The global production of sorbitol has grown from 650 kt in 1992[255] to 700 kt/year by chemical conversion of glucose.[249] About 80% of the latter amount accounts for liquid sorbitol, the remainder is associated to crystal sorbitol. The leading sorbitol production companies worldwide are Cargill, Roquette Freres and Acher Daniels Midland, which together produced approximately 70% of sorbitol volumes in 2013. Depending on the amount produced, the global market value of liquid and syrup sorbitols spans from € 0.8 to 1.2/kg, whereas the value of solid grades is in the range of € 1.6 – 2.2/kg.[255] It is expected that the market value of sorbitol will reach € 3 400 million by 2020.[256]

2.6.2 Xylitol

Xylitol is a C_5-sugar alcohol obtained only from biomass-based pentoses, since it has no petrochemical alternative. This sugar alcohol is broadly used in the food, odontological, and pharmaceutical industries due to the characteristic advantages of polyalcohols. Furthermore, it has been employed to prevent acute otitis in small children[257] and to replace sugar in food and beverages for people with diabetes,[258] due to its comparable sweetness to sucrose.

Xylitol is manufactured industrially by catalytic hydrogenation of xylose. Even though biotechnological advances have been studied to replace the chemical process, it is not yet possible on a large scale. The catalytic conversion of xylose into xylitol is associated with the presence of a metallic catalyst (typically Raney nickel) at high temperatures (373-418 K) and elevated

pressure conditions up to 5066 kPa (Figure 10). Xylitol can also be microbial produced from glucose[259] and cellobiose.[260] Nevertheless, several biochemical reductions have also been reported. Xylitol can also be synthesized with a Ruthenium-based catalyst under extreme operating conditions,[261] which increase the production cost and market price of xylitol. Contrastingly, biotechnical production is increasing in importance because it offers an alternative without extreme operating conditions. The most promising organisms are *Saccharomyces cerevisiae* and various *Candida* yeasts. *Candida* strains have the advantage of being natural xylose consumers, and better maintain the reduction-oxidation balance necessary for high yield xylitol production. Recently, Park et al.[249] published a review with engineered microorganisms (*i.e. S. cerevisiae*, *C. tropicalis*, *E. coli*) to form xylitol from cellobiose, glucose and xylose with yields >95%.

Morales-Rodriguez et al.[262] developed a model of a downstream process of lignocellulosic biomass conversion into bioethanol and xylitol. This study highlights the potential production of xylitol from a side stream of a bioethanol production plant. The findings show a high potential saving on diesel to produce vapor >10,600 kg/h (€11000 /h) and the possibility to significantly reduce the production of CO_2 in the process.
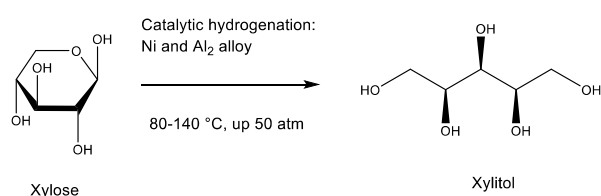
Figure 10. Xylitol production by chemical route. Adapted and reproduced with permission from Ref.[263]. Copyright: 2018 Elsevier.

2.6.2.1 Economic aspects

Xylitol occupies about 15% of the entire global polyalcohol market.[264] By 2012, the global xylitol market reached more than 130 000 tonnes. At that time, the estimated global market was approximately € 293 million per year.[265] In 2016, this value had reached € 625 million and it has been forecasted that by 2022 the global xylitol market will be above € 900 million with an annual production of 267 000 metric tons.[263] The current bulk price varies between 4 and 5 €/kg. The global market of this polyol keeps increasing due to the expansion of chewing gum, care product markets and novel applications in commodity products.

3. Outlook

In this review, we highlight biomass valorization as a significant advantageous area of research for producing value-added products for many applications in various industrial fields. The processes, technicallities and economic feasibility will continue to draw a critical mass of researchers in the proximate future. This is due to the outstanding potential of lignocellulosic biomass as a viable substitute source of fossil fuels to produce chemicals and fuels.[126, 266] In order to accomplish this, biorefeniries need to develop efficient and competitive processes to integrate and produce the various potential chemicals from lignocellulosic biomass.

A significant challenge in heterogeneous catalysis in conversion of lignocellulosic and holocellulosic biomass is that both feedstock and catalysts are in solid states, hence the interaction between them is limited. In order to overcome this solid-solid interaction issue, catalysts have been employed due to their small particle sizes and their affinity in aqueous media, but they can still be recovered by filtration/centrifugation. Nonetheless, the catalyst

separation step faces remaining challenges, mostly due to the presence of the humins that cling to the catalyst surface.[267] Complex biomass feedstocks (e.g. ligning) are difficult to include in biorefinery process schemes and do not allow straight-forward process schemes. Unfortunately advances in this research area are currently slow and costly.

1. Many of the processes highlighted in this review are still early in their development, and major efforts from researchers and industry need to tackle issues regarding separation and scale-up planning. The next natural step is a significant progression of economically feasible processes for transforming lignocellulosic biomass raw materials into viable industrial opportunities.

2. A more thorough understanding of processes, reaction mechanisms, available technologies and conversion routes to form and transform these valuable chemical platforms are greatly needed. It will certainly benefit catalyst design and optimization for specific systems. Moreover, highly active, reusable and hydrothermally stable systems are required to handle these complex chemistries.

3. The high yield of coke, humins and other undesired side-products represents a big challenge for biorefinery systems. An interesting approach is to avoid their formation by implementing biphasic systems. Pretreatment processes as well as separation systems require improvement. Another alternative is to take advantage of the rising markets that humins can have applications in.

4. These pathways have what it takes to lessen the atmospheric CO_2 burden without compromising food supplies. In this regard, bio-based platform molecules offer an interesting and appealing commencement point to carry out the biomass valorization concept and facilitate the currently needed biorefinery paradigm.

5. In regards to economic aspects, as markets expand and new technologies develop, costs tend to decrease. The current stage sets pretreatment technologies and dependency of oil as the main bottlenecks for attractive investments in the biomass-based sector, which need to be addressed.

6. Proper scale-up simulations need to be introduced and studied in order to better understand the intricacies involved. The evolution of lab to commercial plant handling lignocellulosic feedstock faces several issues that could be avoided with strong planning and research.

4. Conclusions

The catalytic conversion of lignocellulosic biomass into value-added chemicals and fuels is a formidable alternative and can lighten many of the adverse issues related with non-renewable sources. The major aim of this work has been to point out and illustrate a series of general examples of the application possibilities of catalysts and their development. Hopefully the readers have received a broad and compelling overview of the different routes to efficiently produce value-added chemicals from holocellulosic biomass, that could substitute fossil-based products, and the key platform molecules bearing a great potential for future development. In order to further improve the integrated processes for lignocellulosic biomass processing to produce the desired chemicals, it is necessary to overcome the tasks ahead. The main challenges to develop an efficient catalytic conversion of biomass calls for: hydrothermally stable solid catalysts, efficient pretreatment processes for biomass, less-toxic catalysts, selectivity increases for desired products, and deeper understanding of the reaction chemistry to cover the way to a

widespread implementation of biorefineries. In any case, the future of chemistry in this relevant field is highly promising. The next steps have to be focused on expanding and developing the integration of catalytic environmentally-balanced processes for lignocellulosic raw materials. For this, researchers and industry have to collaborate closely to reach efficient
 scale-up and further commercialization.

Acknowledgements

Keywords: lignocellulosic biomass • catalytic conversion • furfural • value-added platform molecules • biorefinery

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