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Role of Biomass in the Production of Chemicals

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1.1 Introduction

Chemistry is a fundamental part of everything around us. Nature is largely responsible for all of the chemistry that occurs and has been so from the dawn of time. However, societal advances and technological developments in recent years have allowed us to contribute far more chemistry than in the past. Quality-of-life improvements for major parts of the world with better food distribution, clothing, technological devices, and medical treatments have required the chemistry to progress further with detrimental unknown effects on the environment. Policies and scientists worldwide are now striving toward the development of a truly sustainable society, culminating into the implementation of the UN's 17 Sustainable Development Goals that tackle various issues including infrastructures, education, equality, peace, and environmental protection [1]. In the active search for solutions, biomass valorization has emerged as the most viable option for a more sustainable chemical industry.

The impact that sustainability could have on the chemical industry is best reflected in the magnitude of the chemical industry itself. Today, the chemical industry generates approximately $4 trillion in global sales with the production of more than 95% of all commodities [2]. One of the biggest turning points in the chemical industry, and what arguably led it to such heights, was the advent of catalytic cracking in the nineteenth century for the refining of fossil resources. Catalytic cracking allowed for most of the products we use daily to be easily sourced from petroleum [3]. Biomass valorization processes were also being explored around the same time. However, the complex nature of biomass and the wide availability of fossil resources gained all of society's attention on the use of the latter [4]. As such, petroleum processes have been the major focus of scientists and engineers for the past two centuries. Although significant developments have been achieved considering this with higher resource efficiency and cleaner technologies, the resulting environmental concerns driven by the emissions and spills have led much attention back to renewable processes such as biomass valorization.

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Biomass valorization and more sustainable practices are important steps for overturning the “disposable society” mindset where resources are viewed as infinite, cheap, and harmless. One of the most straightforward examples of this can be seen with plastic. Advances in chemistry not only created plastics but also helped notice the alarming consequences.

Plastics were developed in conjunction with the advent of petroleum processes. Plastic products possess desirable characteristics (lightweight, durable, etc.) that allow for endless applications at a low manufacturing cost. Plastics found their way into daily use with things such as clothing and packaging. However, we were unequipped to properly handle this new technology. The characteristics that make plastic so appealing for a wide variety of applications (i.e. durable and heat resistant) are the same that make plastic so difficult to deal with. Its inherent non-degradability, along with extremely careless handling and littering, created a plastic waste crisis with the now widespread problem of microplastics in our oceans [5, 6]. Biomass is a more attractive feedstock that can create bio-based and/or biodegradable plastics to help overturn the drastic impact from petroleum-based products. Much initial research has focused on using biomass for *drop-in* solutions, i.e. plastics with the same composition and properties as the traditional ones (e.g. polyethylene [PE] and polyethylene terephthalate [PET]). However, the process chemistry limits the efficiency to sugars. On the other hand, other bio-based plastics with new properties have been developed, e.g. polyethylene furanoate (PEF) or poly-lactate (PLA). The former is a durable plastic based on furan and the latter a compostable plastic. Developing bio-based plastics that are also biodegradable – a fundamental challenge in biomass valorization – can ensure a higher sustainability at the waste management stage, as their waste is less dangerous to animals and humans (microplastics, trapped in fishing nets). However, differentiation in the lifetimes of plastics will also require the development of durable bioplastics.

Accumulating plastic waste is just one of the many concerns that is helping to drive sustainable practices forward. Other concerns from the fossil-driven industrial revolution include the following:

- Irreversible depletion of fossil fuels (i.e. oil and gas) and their detrimental environmental issues [7, 8].
- Higher average temperatures and aggravation of weather conditions worldwide (e.g. heavier rains) from an increase of greenhouse gases and record levels of CO_2 in the atmosphere [9].
- Global population growth (>9 billion projected by 2050) leading to higher energy, food, and chemical demands [10].

These concerns require a sustainable chemical industry that embraces the concepts of *green chemistry* [11], *circular* [12] and *low-carbon economies* [13], and high *resource efficiency* [14]. As such, biomass valorization and conversion of renewable feedstocks through green processes are advancing to fully shift toward a safer and sustainable chemical industry.

1.2 Biomass Valorization

The sustainable production of chemicals and products can be achieved from conversion of biomass, an inherently renewable source. Biomass covers a wide range of bio-based resources from plants or animals. These resources include plant-based materials, biowastes, and aquatic organisms. Valorizing renewable biomass feedstocks can offer environmental benefits that include reduced emissions, safer feedstocks, better geographic distribution of resources, and achievement of a circular economy [12, 15–18].

In a circular economy, resources – such as carbon, nitrogen, and phosphorous compounds – are used with a circular "take–make–reuse/recycle" approach, as opposed to a linear "take–make–dispose" approach [12]. A closed cycle can be achieved with biomass valorization processes by recycling the generated CO_2 through natural photosynthetic processes [19, 20]. This process happens particularly with biodegradable plastics. Further, the existence of nonedible and rapidly growing plants parallel to the development of high-throughput agricultural technologies can lead to a carbon-neutral cycle in short periods of time, readjusting the increased levels of CO_2 emission given by the fossil industries [21].

In the context of biofuels, biomass has been subdivided in three categories given as follows along with the major evidenced drawbacks:

(1) *First-generation biomass:* This includes all edible biomasses (e.g. sugarcane, corn, whey, barley, and sugar beet) that are composed of sucrose or starchy carbohydrates, hence relatively simple macromolecules with low recalcitrance. Biological fermentation of said sugar polymers yields bioethanol, one of the most studied drop-in biofuels with current industrial production [22]. Food-derived vegetable oils are also considered as first-generation biomass and they yield biodiesel through transesterification [23]. The main issue of this type of biomass is the clear competition with food resources (which will be continuously more precious, given the increase of world population) as well as the intensive use of water and land for the growth of said crops [24].

(2) *Second-generation biomass*: Nonfood raw materials, including by-products and waste materials. Generally, second-generation biofuels are produced from lignocelluloses (e.g. grasses, soft or hard wood, and forestry residues) or various wastes/by-products (e.g. *agricultural*: stover, wheat straw, corn cob, rice husk, and sugarcane bagasse; *industrial*: glycerol, grains from distilleries, and paper sludge; or *urban*: household and municipal solid wastes). Given the structural composition of these feedstocks (mixtures of cellulose, hemicellulose, and lignin), pretreatment is usually required for fermentation to biofuels and biochemicals, and the process economics are hindered by the use of multiple steps, leading to lower overall conversions [25–30]. The main technological challenge of these feedstocks is, in fact, the structural complexity that hinders the efficient use of the lignocelluloses as a whole, calling for pretreatments that in turn possess drawbacks depending on the method (vide infra).

(3) *Third-generation biomass*: This includes nonedible feedstocks that do not require agricultural lands for their cultivation, namely, aquatic biomass, such as algae and other microorganisms (e.g. cyanobacteria). Depending on the strain, these feedstocks may contain mono/polyunsaturated hydrocarbons to produce gasoline-like fuels via cracking or higher lipid content for biodiesel applications via transesterification. When considering algae, the main issue is correlated with the high water content that hinders transportation or requires significant energy inputs or long times to dry them, whereas microorganisms require specific operating conditions. Furthermore, the economic challenges of these feedstocks limit their industrial application, given the low cultivation volumes and resource efficiency in processing [31–33].

A fourth generation of biomass is also contemplated and exemplified as modified microorganisms considered in the third generation, finally used to harvest solar energy through photosynthetic processes [34, 35]. However, these microbial species require improvements of genomics-based breeding and carry the usual concerns of modified organisms, such as unexpected microbial resistance.

The available volumes of these types of biomass will play a major role in identifying the biggest driver for chemical sustainability. According to a 2018 report from the European Union (EU), the annual production of agricultural biomass (i.e. first generation) was estimated at 956 million tonnes (Mt) of dry matter of which 54% directly used for food consumption and 46% of residues (e.g. leaves and stems) partially used for animal bedding or bioenergy production. In fact, 80% of the agricultural biomass is used as food and feed, showing the limited potential of using first-generation biomass for chemicals and energy production. As it concerns third-generation biomass, in particular algae (including macro and micro), only 0.23 Mt of wet matter was estimated, corresponding to a mere 0.027 Mt of dry mass. On the other hand, the total woody biomass (above ground, second generation) was estimated at 18 600 Mt of dry weight [36]. Looking at the quantities of the different biomasses, the high availability of lignocelluloses in Europe makes them the most attractive. The >18 000 Mt of woody resources can make Europe competitive worldwide and support sustainable processes. Particularly, the efficient use of lignocelluloses and residues would improve the long-term sustainability of the chemical industry, given the volumes and little impact on the food resources, although these feedstocks still rely on forest management constraints. Other waste materials (e.g. food and municipal) are increasing in volumes, given the concomitant increase of world population and improvement of their living conditions. For example, 61 Mt of food waste are produced yearly in the EU alone [37]. However, the major challenges of these products are the variable seasonal composition as well as the implementation of a proper supply chain of these anthropological side streams to biorefineries [38].

Conversion strategies of biomass, however, generally come with low resource efficiency, causing higher production costs and limited competitiveness with the well-established petroleum market. Thus, for economic advantage, high volumes, ease of production, and limited competition with other markets (e.g. food) are required. In this sense, the use of lignocellulosic biomass may again offer a promising alternative to the fossil-based industry. From an energetic perspective, lignocelluloses and other waste materials possess lower energy densities compared to nonrenewable resources such as coal, oil, and natural gas. However, biopower possesses negative emissions thanks to the photosynthetic process, whereas fossil fuels cause significant life cycle greenhouse gas emissions [39]. Also, conversion of biomass to key molecules (e.g. ethanol, 2-methylfuran, and hydrogenated ethers and fatty acids) can offer biofuel diversification with various energy contents for different transport applications, including aviation; these processes rely on the separation of the different biomass components [21, 40]. From a chemical point of view, the use of lignocelluloses can offer a wide variety of platform chemicals for the synthesis of not only traditional but also new products to satisfy different areas in the chemical industry (pharmaceuticals, textiles, and materials), which are discussed in the following paragraph. A separation of bio-components will be required and explained therein.

1.3 Lignocellulosic Biomass

Of all types of biomass, lignocelluloses are the most available on the planet, ranging from wood and forestry waste to straw and agricultural waste. Lignocellulosic biomass is composed of cellulose (40–50%), hemicellulose (15–20%), lignin (25–35%), and other elements (Figure 1.1). Both cellulose and hemicellulose are carbohydrate-based polymers, while lignin is an aromatic polymer. Cellulose is a linear, glucose-based polymer, making it a good source of this C6-sugar. Cellulose cross-links with hemicellulose, a branched polymer composed of different C5-carbohydrates, uronic acids, and C6-sugars. Lignin, perhaps the most irregular component of lignocellulose, is a polyaromatic macromolecule composed of phenylpropane derivatives. Lignin is mostly responsible for structural rigidity within the

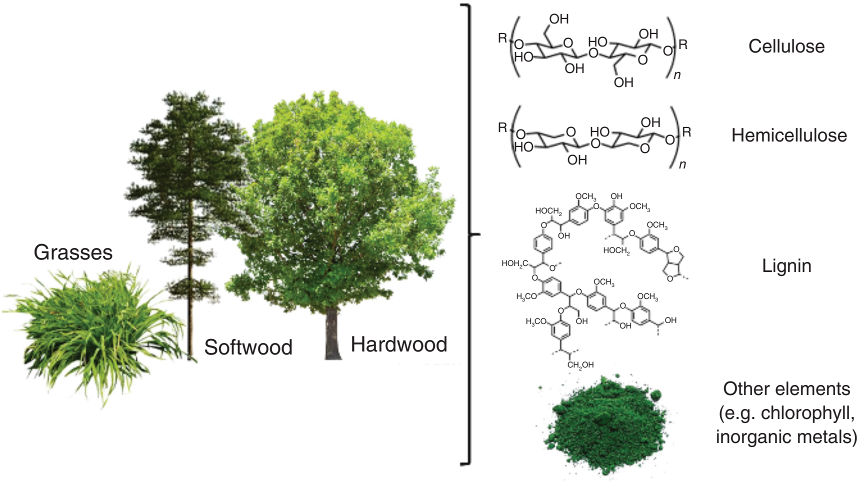

Figure 1.1 Schematic representation of the components of lignocelluloses.

lignocellulose. Further, lignocellulosic bio-feedstocks include variable quantities of pigments; terpenes; inorganic elements such as Mn, K, P, Cl, Ca, Mg, and Na, as well as Al, C, Fe, N, S, Si, and Ti to a smaller extent; and various extractives, e.g. carbohydrates, proteins, lipids, waxes, chlorophyll, terpenes, tannins, and uronic acids.

An extensive and systematic review on the composition of various types of biomass shows the significant changes in the composition of these elements depending on the type of biomass [41].

Overall, lignocelluloses are made of highly oxygenated C5- and C6-derivatives. The oxygen functionalities make lignocelluloses a much different feedstock to petroleum sources that are mainly hydrocarbons. The oxygen functionalities in lignocelluloses are in some cases advantageous because they can minimize oxidation reactions, which usually have a negative environmental impact, and favor reduction reactions, which are typically milder processes and have less environmental impact. Further, the propensity to produce coke/humins and ash obliges the use of mild temperatures for these by-products' minimization, as opposed to the traditional catalytic cracking/reforming of fossils. In fact, the presence of plenty of oxygen functionalities and low volatility tend to lead to the molecules' decomposition at high temperatures, generating carbonaceous residues.

Lignocelluloses have variable composition in their singular components depending on the plant origin. Water and inorganic residue contents also vary significantly from grass to wood. Although composition does vary significantly, biomass can source several useful compounds, including carbohydrates, aromatics, terpene, and fatty esters. These different components can be isolated and converted for use in many applications including pharmaceutical, cosmetics/perfumes, plastics, textiles, and specialty chemicals. For this, several different biomass valorization routes can be envisioned with a wide range of obtainable products.

1.4 Key Biomolecules

During the first attempts of biomass valorization, *drop-in* energy solutions have been investigated as they could directly substitute the use of fossil resources for transportation vehicles. The most common examples are the use of bioethanol and biodiesel as additives to common automotive fuels. Bioethanol is mostly produced in industry using yeast fermentation of C6-sugars. With an increase of 25 billion gallons (roughly 75 Mt) worldwide, bioethanol is one of the most mass-produced bio-based molecules. However, starchy feedstocks (i.e. first generation) are mostly used in the production of bioethanol, causing direct competition with the food market, widespread deforestation, and concerns on the presence of enough food sources for both humans and animals [42]. Also, bioethanol has limited competitiveness with petroleum options because of low product value and relatively high price, especially when considering food sustainability. To add perspective, the price of oil would have to be above \$70–80 per barrel for bioethanol to be competitive from a cost standpoint, while today, oil is at <\$40 per barrel [43].

Alternatively, another approach is to obtain different platform molecules from biomass that can be used for production of a wide variety of chemicals. With a shift on how we perceive platform molecules, new chemical (and biological) pathways can be envisioned. In order to induce this shift, several important bio-products unique from petrol-based ones were identified in a 2004 US Department of Energy report [44] later updated by Bozell and Petersen [45] and further reviewed by Gallezot [46]. Bio-based platform chemical families and their respective processes, industrial applications and current technical challenges, are summarized in Table 1.1 [44–47]. For more information on the industrial challenges for biomass valorization, the reader is referred to Chapter 13 of this book.

Table 1.1 represents only a small fraction of all the molecules that could be identified as valuable platform chemicals, opening a significant number of possibilities for the synthesis of petrol-like or new molecules. However, apart from established processes such as those of sorbitol and glycerol, all other biomolecules generally suffer from high production costs that might be caused by

(i) high price of feedstocks (depending on the required sugar purity).
(ii) low resource efficiency (e.g. synthesis of by-products that lower conversions and intensify purification/separation processes).
(iii) high investment and operational cost required for the reactor volumes or design, or need to maintain sterile conditions during production.
(iv) inefficient catalysts, which could be *(a) biological* (enzyme and bacteria), which require metabolic engineering for higher efficiency and durability; *(b) homogeneous*, which tend to be corrosive, toxic, or difficult to reuse and recycle; or *(c) heterogeneous*, which have lower conversions even if they can be recovered and reused, but are prone to irreversible adsorption of organic molecules, leading to coke and thus reactor fouling.

Particularly, when compared to petrol-like compounds, the disadvantages of chemicals from biomass processing become increasingly apparent in terms of overall costs. Even when only considering feedstock transportation, the advantage goes to petroleum, as it is a fluid that can be pumped (or natural gas through pipelines). Biomass tends to occupy larger volumes, given its physical nature, and is much more difficult to transport as a result. Nevertheless, the most notable difference that gives petrol-like compounds the slight edge is the absence of oxygen functionalities (aliphatics/aromatics/olefins), which reduces their reactivity but yields larger production volumes by the addition of heteroatoms. In fact, although fossil compounds are modified via oxidation, bio-derived compounds often require oxygen removal. In this sense, larger initial volumes are required for biomass to reach the same final product volume, making it economically inefficient. Moreover, the reactivity of oxygen groups in biomass gives inefficient processes, especially if targeting petrol-like compounds. In this regard, a better route is to build off these different functionalities and explore new platform chemicals that are specific for biomass products. Most of the advances have been achieved largely because of catalytic pathways that allow for lower energy requirements and higher resource efficiency.

Table 1.1 Key examples of the possible bio-based products, state-of-the-art processes, and challenges [44–47].

Bio-product platform (example)	Process	Industrial application	Technological challenge
1,4-Diacid (succinic acid)	Anaerobic fermentation	Pharmaceutical, food, polymers, solvents	Separation/purification of products
Furanics (HMF)	Acid-catalyzed dehydration of C-5 and C-6 sugars/oxidation	Food/cosmetics, polymers, construction, textiles, fuels	Low resource efficiency
3-Hydroxypropionic acid (acrylic acid)	Aerobic fermentation	Polymers, textiles	Low resource efficiency Under metabolic engineering research
Amino acid (aspartic and glutamic acids)	Microbial process	Biodegradable polymers, pharmaceuticals	Need of sterile conditions Complex separation Under metabolic engineering research
Gluconic acid (methylglucoside)	Aerobic fermentation/catalytic oxidation	Food, pharmaceuticals	Low resource efficiency/catalyst deactivation
Itaconic acid (itaconic anhydride)	Aerobic fermentation	Specialty polymers (including biodegradable)	Low resource efficiency Under metabolic engineering research
Glycerol (dihydroxyacetone)	By-product of biodiesel/soap manufacture	Cosmetics, food, pharmaceuticals, lubricants, polymers, Li batteries	Low market price Expensive purification Catalyst separation/deactivation in upgrade
Levulinates (γ-valerolactone)	Acid-catalyzed dehydration of C-6 sugars	Fragrances, food, fuels, solvents, pharmaceuticals, polymers	Low resource efficiency
Sorbitol (isosorbide)	Hydrogenation of C-6 sugars	Food, pharmaceuticals	Established technology Low market price
Lactones (3-hydroxy-butyrolactone)	Oxidative degradation of C-5 and C-6 sugars	Pharmaceuticals, chiral building block, polymers	Inefficient oxidation Low resource efficiency unless starch is used Inhibitory effect of biomass
Lactic acid (oxalic acid)	Anaerobic fermentation	Cosmetics, pharmaceutical, biodegradable polymers	High feedstock cost (high-purity lignocellulosic sugars or food derived) Separation/purification of products

(*continued*)

Table 1.1 (Continued)

Bio-product platform (example)	Process	Industrial application	Technological challenge
Biohydrocarbons (isoprene)	Aerobic fermentation	Polymers	Investment cost (reactors) High feedstock cost (high-purity lignocellulosic sugars or food derived)
ABE (acetone, butanol, ethanol)	ABE fermentation	Fuels, solvents	High feedstock cost Low resource efficiency
Lignin	Catalytic decomposition	Polymers, food, pharmaceuticals, fuels	Low resource efficiency

Sources: Werpy et al. [44], Bozell et al. [45], Gallezot [46], Isikgor et al. [47].

For instance, by taking the case study of plastic production from biomass, a variety of options can be imagined [47], giving strong environmental benefits. If traditional plastics (e.g. PE, polyamides, and PET) are produced starting from biomass, a possible reduction of ca. 310 Mt of CO_2-equiv per year could be achieved with the substitution of less than 66% of the current fossil-based plastics [48]. This footprint reduction is solely based on the process and not on the product as the degradation characteristics of these plastics (i.e. nonbiodegradable) are the same regardless of the feedstock type (e.g. biomass and petroleum). At the same time, new and innovative platform chemicals can be produced with fewer chemical steps (e.g. furanics as opposed to aromatics), opening new opportunities in the production of bio-based plastics. For instance, a furan-based plastic was synthesized via the polymerization of 2,5-furandicarboxylic acid (FDCA), an oxidized product of 5-hydroxymethylfurfural (HMF) (see Table 1.1), and ethylene glycol [49, 50]. This plastic, known as polyethylene furanoate (PEF), can be conceived as the bio-based parallelism of the common PET, where the C-6 aromatic functionality is substituted by a furan ring. Further, the furan-based polymer was found to perform better compared to PET in terms of physical properties such as gas barrier [49]. The production of PEF relies on the acid-catalyzed dehydration of lignocellulosic biomass and/or sugars (e.g. glucose) into HMF with subsequent oxidation to FDCA (Figure 1.2) (see further Chapter 13).

However, this process is hindered by the coproduction of substances known as humins (at times, referred to as coke) in the dehydration step [51–53]. The lower resource efficiency of the first step increases the overall cost of PEF, limiting its competition with fossil-based PET regardless of the improved properties. This low atom economy is common to many bio-based processes.

Generally, when producing chemicals from whole lignocelluloses, the yields of conversion processes are lower compared to the same synthesis starting from the sugar (e.g. fructose, xylose, and glucose); hence, process costs tend to increase. Predominantly, the differences of lignin content and feedstock density depending on the considered biomass (e.g. grasses vs. softwood vs. hardwood) cause variation on the process yields as well as the amount of volumes to be processed (e.g. grasses

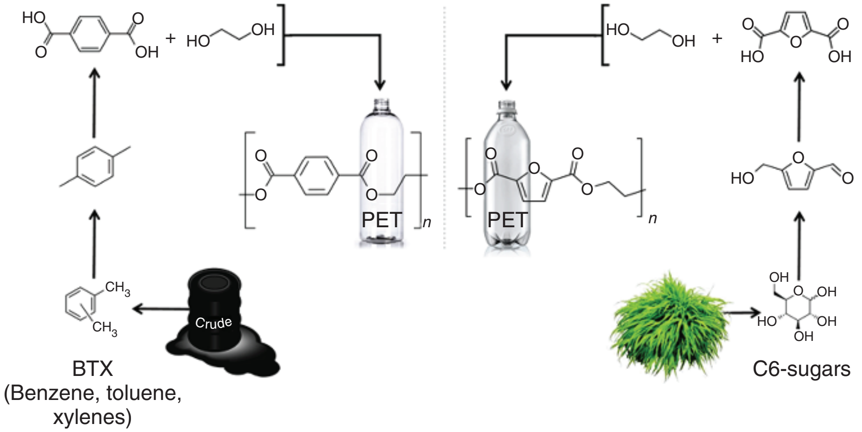

Figure 1.2 Parallelism between the production of PET (left) and PEF (right).

require bigger volumes). In particular, the hydrogen bonding between the different components (i.e. lignin, hemicellulose, and cellulose) reduces the available surface to processing, increasing the structural complexity and the recalcitrant nature of lignocellulosic feedstocks. Furthermore, the inorganic metals (e.g. Mg and Ca) naturally present in plants may induce reactor fouling by induced precipitation of salts or heterogeneous catalyst (e.g. zeolites) deactivation by ion exchange [54, 55]. Above all, the aforementioned large presence of heteroatoms (particularly oxygen) increases the moieties' reactivity, leading to low atom efficiency and occurrence of undesired side reactions, such as the synthesis of humins that act as a catalyst deactivator (in a similar way to coke) and promote reactor fouling.

In order to overcome these challenges, strategies include the use of unconventional solvents, milder conditions, and various pretreatment methods in order to separate the single components (e.g. decompose cellulose to glucose) and allow targeted valorization.

1.5 Solvents

Solvent selection is an important factor in the viability of biomass processes. Aqueous solvents are advantageous for high solubility with most biomass feedstocks. Other desirable factors of aqueous solvents are low cost and low environmental impact, especially when compared to other solvents. Water, for instance, is the ideal solvent for biocatalytic routes as they have fewer chances to denature the used microorganism [56]. However, a downside of using water is usually the higher energy-intensive separation processes, hence higher cost [57]. From the chemical point of view, aqueous solvents typically facilitate many side reactions that lower yields, including decomposition and polymerization [58–61]. In fact, many of the mechanisms of humin formation (i.e. sugar platform chemical polymer with low current market value) are attributed to ring-opening hydrolysis [62]. The use of organic solvents can overcome this type of mechanism and maintain a low environmental impact if the process is designed to recycle said solvents. Polar aprotic solvents can offer higher yields of the desired products compared to aqueous systems thanks to high sugar solubility and suppression of side reactions [63, 64]. However, most polar aprotic solvents, such as dimethyl sulfoxide (DMSO), have high boiling points that make product separation more difficult and significantly increase production costs.

Other conventional solvents have certainly been employed in biomass applications as well, but focus has been placed on coupling biomass processes with bio-based or green solvents. These include bio-based conventional solvents, terpenes, ionic liquids, switchable solvents, fatty acid/glycerol-based solvents, and liquid carbon dioxide.

Conventional bio-based solvents can mostly be used as a *drop-in* replacement. Common examples of this are glycerol, ethyl lactate, and 2-methyltetrahydrofuran. In addition, acetone and various linear alcohols (e.g. methanol, ethanol, and butanol) can be derived from bio-based sources, but current technology is not the most efficient [65]. The use of these solvents may offer an advantage, given the chemical affinity to the desired platform biomolecules. These solvents alone, however, have also induced the formation of humins.

Terpenes can be extracted from various materials in nature and subsequently used as a bio-based solvent. *Cis*-rich pinane can be extracted from pine tree by-products and used as a suitable replacement for *n*-hexane [66]. Another example, D-limonene, has similar properties and comes from orange peels. It has been safely designated by the USFDA for use in home and personal products [65]. However, the small volumes of these potential solvents limit their use to specialty applications (e.g. cosmetics).

Ionic liquids (ILs) are also being explored as solvents for biomass processes. Recently, they have been a major focus in biomass applications for their potential to overcome other solvent limitations because of their versatility (i.e. large working temperature range, acidic or basic capabilities, and compatibility with different materials) and non-volatility. Initial studies show that ionic liquids can offer satisfactory product yields when combined with metal halides. In fact, whereas the ionic liquid provides a stable medium for sugar conversion, the halide acts as Brønsted acid catalyzing the system. Another advantage of using ionic liquids is that they are generally considered to have high stability. However, application of ionic liquids is still a relatively new field and the physicochemical properties are not properly defined, in the end causing safety concerns [67]. The major issue related to the use of ionic liquids, however, is the hindered separation of oxygenated products such as furanics, given the higher stability of these molecules in charged media [68].

Switchable solvents are attractive for coupling desirable solvent properties that would otherwise be on the opposite ends of the spectrum. Switchable solvents are able to quickly undergo reversible property switches that are activated by an external change. The external trigger is typically a change in pH, temperature or concentration [65]. Switchable solvents are like biphasic solvents in that they both can possess two different solvent properties in just one system. One highly desirable solvent property for manipulation is hydrophilic character [69]. A switchable hydrophilic solvent (SHS) has been used for extracting different fractions such as proteins, lipids, and carbohydrates from microalgal biomass [69] and also for extracting phenols from lignin pyrolysis oil [70]. The SHS employed in both of these studies was *N,N*-dimethylcyclohexylamine [69, 70]. However, limitations are present with switchable solvents as it is a newer field lacking in research.

Other solvents worth noting are fatty acid/glycerol-based solvents, advantageous for chemical inertness, and liquid/supercritical CO_2, advantageous for wide availability, good solubility, and low toxicity [65]. The high boiling point of the glycerol mixtures (higher than DMSO) may be used as an advantage for separating volatile molecules but hinders their recyclability if nonvolatile molecules are coproduced (e.g. humins). Alternatively, employing liquid/supercritical CO_2 as a solvent indicates costly high-pressure systems/vessels and additional safety requirements.

Another solvent approach is the use of biphasic systems. With two different phases, reactions take place in the aqueous phase but extraction and separation in the organic phase [59, 71–74]. Hydrophobic extracting phases (e.g. cyclopentyl methyl ether, CPME) in the presence of a chloride salt (e.g. NaCl) can enhance the partitioning coefficient of the organic solvent, favoring extraction [71]. Otherwise, polar solvents with low water solubility (e.g. methyl isobutyl ketone, MIBK) can be used in the sugar conversions. Even so, the addition of multiple solvents increases the production costs even if recycled (small loss of solvents, specialty molecules) and reduces the *greenness* of the overall process.

By using these (mixtures of) solvents, one-pot transformation of lignocelluloses via different methodologies has been attempted [50]. However, one-step procedures are difficult to achieve with biomass processes because of the intricacies associated with solvent selection, catalyst, and other operating conditions. With this in mind, biomass processes that focus on individual bio-components as opposed to entire systems could be more effective.

1.6 Pretreatment of Lignocelluloses

Pretreatment is a necessary measure for handling biomass on an individual component basis. One of the main functions for pretreatment is to facilitate separation and allow for improved access of the different biomass fractions, particularly from the rigid components that make up the plant wall [75]. In lignocellulose, these rigid components that significantly hinder solubilization are lignin and cellulose. Peculiarly, the separation of each bio-component without further decomposition (e.g. to by-products) could greatly contribute to the development of efficient conversion strategies, improving the competitiveness of a bio-economy.

Biomass pretreatments can be classified as physical, chemical, physicochemical, or biological [75–77]. Physical pretreatment is reserved mainly for less complex applications where only an increased surface area is mostly desired. Some common physical pretreatment methods are sheer mixing, milling, and grinding that physically break apart the plant wall components [76]. Chemical pretreatment is widely used for its ability to greatly improve solubilization in order to make subsequent biomass processes possible. Chemical methods include acid/alkali treatment, ozonolysis, and organosolv [77]. Many researchers have been utilizing acid treatment as a simple chemical transformation route that is particularly useful for releasing some of the bio-sugars that are locked behind the more rigid components. Furthermore, if the targeted reaction is acid-catalyzed dehydration of the sugars to furanics or levulinics, the plausible residual presence of acids may only enhance the rate of said reaction. On the other hand, most biological treatments are safe and green processes that utilize fungi or other microorganisms. The enzymes break down hemicellulose and lignin rather well, while leaving intact cellulose. However, biological processes proceed at rather slow rates and the microorganisms typically only thrive in a fine-tuned aqueous environment. A majority of the innovative pretreatment methods fall under physicochemical, as many benefits from the combinatory approach. These combination treatments include steam explosion, ammonia fiber expansion, carbon dioxide explosion, and wet oxidation with steam explosion being one of the most used. Steam explosion uses high-pressure steam that creates a self-reacting autohydrolysis environment for transforming biomass mechanically and chemically [25].

With current progress, pretreatment is a necessary measure for processing lignocellulosic biomass. The lignin content is largely responsible for complicating the heterogeneous nature of lignocelluloses and for contributing recalcitrant properties that make it difficult to handle. Without pretreatment, most valorization approaches are not cost effective [78].

Ideally, a pretreatment step would efficiently separate lignocellulose into its single components. If this is achieved, biomass processes could be standardized (based on each component) to greatly alleviate the issues of biomass inconsistency. It would also contribute to optimized processes that maximize process conditions such as yields and overall costs. When contemplating biocatalytic conversion of biomass (e.g. yeast fermentation), typical yields are low (<20%) without pretreatment. This phenomenon is given by the barrier effect of lignin to enzyme, physically hindering the hydrolysis of the digestible components (i.e. sugars) [79, 80]. Improvements of product yields have been obtained with either biological [81], physical [82], and chemical steps [78, 83] or physicochemical [84, 85] pretreatments, thus giving higher resource efficiency. Cost-effective solutions would ideally remove lignin without affecting the desired carbohydrates, hence being energy effective while having a simple reactor design and low production of waste compounds (including solvents) [86]. Nevertheless, improvement of the current pretreatment technologies is still required to obtain economical solutions. Various pretreatment strategies and their advantages and disadvantages are illustrated in Table 1.2.

Overall, different pretreatment methods will be preferred for different applications. For example, applications requiring low toxicity would be better suited with microbial conversions. Alternatively, applications requiring high sugar yields would probably utilize chemical conversions. The main challenge for selective biomass processes is achieving a reasonable balance between cost considerations and efficient separation of each component. In addition, pretreatment requirements with current technologies further complicate the processes [87]. Innovative solutions

Table 1.2 Advantages and disadvantages of pretreatment methods for lignocelluloses.

Method	Pretreatment	Advantages	Disadvantages
Biological	Fungi	Energy effective Degrades lignin/hemicellulose network	Low hydrolysis rate
Physical	Milling	Reduces cellulose crystallinity	Energy intensive
Chemical	Ozonolysis	Lignin reduction Low microbial inhibitors	Cost ineffective (ozone)
	Organosolv	Lignin and hemicellulose hydrolysis	Big solvent volumes Requires solvent recycle
	Alkali	Lignin removal	Inefficient for softwoods Large amounts of water
		Reduces cellulose crystallinity	Long pretreatment times
		Limited hemicellulose degradation	Base recycle
	Concentrated acid	High glucose yield Energy effective	Large amounts of acids Requires acid recycle Reactor corrosion
	Diluted acid	Low microbial inhibitors Lower corrosion issues	Low sugar yields Degradation products
	Ionic liquids	Reduces cellulose crystallinity	Cost ineffective (ionic liquids)
		Higher accessible surface area	Difficult recovery/separation of desired products
		Lignin removal Degrades lignin/hemicellulose network	Potential toxicity and thermal instability of ionic liquids
Physicochemical	Steam explosion	Lignin removal Hemicellulose solubilization	High microbial inhibitors
		Fair sugar yields Economical	Partial hemicellulose degradation
	Ammonia fiber expansion (AFEX)	Higher accessible surface area	Inefficient with lignin-rich biomass
		Low microbial inhibitors	Big ammonia volumes (cost)

(*continued*)

Table 1.2 (Continued)

Method	Pretreatment	Advantages	Disadvantages
	CO_2 explosion	Higher accessible surface area	No effect on lignin/hemicelluloses network
		Low microbial inhibitors Economical	High pressure (cost, reactor)
	Wet oxidation	Lignin removal Low microbial inhibitors Energy effective	Cost ineffective (oxygen and alkaline catalyst)

that address these challenges will help push biomass processes closer to practical implementation.

1.7 Conclusions and Perspectives

The search of a true sustainable chemical industry is driven by the development of processes that rely on not only renewable feedstocks associated with *low environmental impact* techniques but also economic viability to compete with the well-established oil and gas markets. To recede the dependency on polluting resources, creative solutions following a *green* design in the most restringing way are required. The following chapters in this book discuss various methods of biomass valorization, along with their respective challenges and innovative solutions, as means to progress toward chemical sustainability.

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