

The role of biomass pretreatment for sustainable biorefineries

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Pretreatment has been regarded as one of the most critical steps for the development of sustainable biorefineries that are based on lignocellulose conversion processes and this is related to the close association that exists among plant cell wall macromolecular components. Among the many criteria for determining the efficiency of a biomass pretreatment technique, the obtainment of high process yields in fermentable sugars and other useful process streams, the development of substrate accessibility for enzymatic hydrolysis and the minimal release of both hydrolysis and fermentation inhibitors are highly influential. This work summarizes the main principles of the most relevant biomass pretreatment techniques for biorefinery applications.

Key words: lignocellulosic materials, pretreatment, biorefinery, process yields

INTRODUCTION

Biomass recalcitrance is the major obstacle towards the transformation of lignocellulosic materials into valuable products. Several pretreatment techniques have been made available so far for different feedstocks and for different purposes [1-3]. However, choosing the right pretreatment technique requires a broad knowledge about the biomass chemical composition, the process steps to which it will be submitted, and the downstream processing involved in achieving products that satisfy the market demand for quality, yields and environmental impact. Parameters such as process energy balance, capital cost for operations in large scale, ability of being multipurpose in relation to feedstocks and products, cost of the biomass source and environmental implications of the downstream processing must be ideally matched to define a highly efficient, low-cost pretreatment technique for biorefinery applications [4-6]. Therefore, one needs to know the fundamental chemistry and basic engineering of a given pretreatment technique to be able to diversify its application as much as possible to different raw materials and to a variety of desired products.

PRETREATMENT TECHNIQUES FOR OPTIMAL BIOMASS DECONSTRUCTION

The recent trend of transforming conventional industrial facilities to platforms of a wide range of bioproducts using the concept of biorefinery presents an increasing socioeconomic and environmental appeal. In addition, the possibility of

developing biomass production processes following the pillars of circular economy stimulates stakeholders and government funding agencies, targeting further developments to improve the economics of the entire production chain [3, 5-8]. Therefore, several research strategies are being devoted to the development of more efficient conversion processes and to the improvement of those already existing.

The use of renewable biomass for bioproducts or bioenergy applications covers a series of steps from logistics to process optimization biomass harvesting and conditioning, pretreatment, enzymatic hydrolysis, fermentation and ethanol separation [1, 9]. By contrast to first generation ethanol production processes (mostly based on sucrose and starch hydrolysates), pretreatment is a crucial step to reduce the natural recalcitrance of lignocellulosic materials, leading to higher cellulose and hemicellulose availability for hydrolysis and consequently to higher yield monomeric sugars yields for fermentation.

Pretreatment techniques range from relatively simple operations such as drying, grinding or milling and sieving, regarded as mechanical or physical pretreatments, to more sophisticated approaches using specialty chemicals and complex unit operations. There is a wide range of mature pretreatment techniques already available and these are based on the use of diluted acids, alkali, ammonia, ionic liquids (ILs), organic solvents, liquid hot water and supercritical fluids, just to name a few [3, 6, 10-12]. Currently, many research groups are exploring this research topic and several elegant bibliographic reviews have been made available in the literature [1, 13-17].

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Beyond recalcitrance minimization for the efficient enzymatic hydrolysis of plant cell wall glucans (mostly cellulose), pretreatment can also allow for the recovery of desired co-products, such as extractives, hemicelluloses, oligomers and specially lignin. Lignin is a biopolymer that stands out as a rich matrix for the production of numerous high value-added products for energy or fine chemical applications [18-20].

Broadly speaking, pretreatment techniques are classified into physical, chemical, physicochemical, biological or hybrid processes in which two or more of these options are combined [9, 21, 22]. By contrast, some authors prefer to classify pretreatment approaches according to their effect on biomass structure, that is, size reduction,

dissolution, hydrolysis, oxidation, reactive extraction or biodegradation [14, 23, 24]. Additionally, there is a classification based on pretreatment pH (alkaline, acid or neutral) [25]. Indeed, achieving a highly effective biomass fractionation by employing one single pretreatment technique is a difficult task and still a great industrial challenge. Therefore, a combined approach is highly recommended to achieve high yields of cellulose fibers, sugar monomers and lignin among other biobased products of interest [8, 26, 27]. Table 1 describes some of the most important pretreatment techniques according to their broad classification and provides details about their main effect on the macromolecular organization of lignocellulosic materials.

Table 1. The main pretreatment techniques applied to lignocellulosic materials.

Process	Description
BIOLOGICAL	Fungi Lignin biodegradation by laccases and manganese peroxidases. High selectivity at very long pretreatment times
	Bacteria Genetically modified organisms that are able to convert biomass into fuels and chemicals (consolidated bioprocessing)
	Enzymes Selective removal of high molar mass components in cellulosic matrices using lipases, lignin-degrading enzymes and hydrolases
PHYSICAL	Milling Reduction of particle size and increase in substrate surface area for biological or chemical conversion processes
	Microwave Disruption and swelling facilitating hemicelluloses and lignin removal; heating and reaction times are greatly reduced
	Ultrasound Structure modification by cavitation; bonds in lignin-carbohydrate complexes are cleaved by radical chemistry
CHEMICAL	Concentrated acid hydrolysis Cellulose swelling and partial hemicellulose hydrolysis; lignin coalescence and condensation
	Dilute acid hydrolysis Cellulose accessibility increased by partial hemicellulose removal; lignin coalescence, fragmentation and condensation
	Alkaline extraction Lignin extraction and partial hydrolysis of aryl-ether bonds, reducing its average molar mass
	Ionic liquids Carbohydrate or lignin extraction due to its high polarity and strong intermolecular interactions with the cellulosic matrix
	Oxidation Delignification with strong oxidants such as hypochlorite, oxygen radicals and ozone
	Supercritical CO ₂ Partial acid hydrolysis of hemicelluloses, increase in substrate pore volume and available surface area
COMBINED	Organosolv Selective biomass delignification, whose efficiency can be increased by adding an exogenous acid catalyst
	Kraft pulping Alkaline delignification of lignocellulose at ~170 °C using aqueous Na ₂ S/NaOH to isolate cellulose fibers (holocellulose)
	Sulfite pulping Acid delignification at ~160 °C using sulfite/bisulfite species to isolate almost pure cellulose fibers and lignin as lignosulfonate
	SPORL Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose, developed from sulfite pulping to improve enzymatic hydrolysis
	AFEX Partial removal of hemicelluloses and lignin plus changes in the crystalline state of cellulose (from I to III)
	Hydrothermal pretreatment Hemicellulose removal and lignin fragmentation and redistribution by autohydrolysis, increasing cellulose accessibility to enzymatic hydrolysis and hemicellulose recovery mostly as water-soluble oligosaccharides
	Liquid hot water Acid hydrolysis of hemicelluloses and lignin modification and redistribution; may be assisted by acid or basic catalysts
Steam explosion	

Disrupting the cell wall to facilitate enzymatic hydrolysis without sugar degradation and generation of fermentation inhibitors is the main goal of an ideal pretreatment. As described in literature [9, 28], the assessment of biomass pretreatment processes is complex and depends on several factors including (i) the total amount of recoverable carbohydrates (monomers and oligomers released in the liquid phase and polysaccharides retained in the water-insoluble solids); (ii) the accessibility of either unwashed or water-washed pretreatment solids to enzymatic hydrolysis; (iii) the fermentability of pretreatment hydrolysates (C5 stream), diluted or concentrated, targeting microbial growth and process yields; (iv) the fermentability of enzymatic hydrolysates from whole slurries or water-washed pretreatment solids; and (v) the assessment of additional chemical/biotechnological applications of the pretreated fractions for the development of high value-added coproducts [9, 28].

Pretreatment has been recognized as the most important step towards the development of sustainable biomass conversion processes such as cellulosic ethanol production. Biomass cultivation, harvesting and preconditioning, enzymatic hydrolysis, fermentation and product recovery are all very important as well, but none of them matches the strategic planning involved in choosing the best pretreatment and its ideal operational conditions for a given biomass type [8, 10]. Under the biorefinery concept, pretreatment is critical to determine how agnostic is the conversion technology regarding the biomass source and its presentation, with details such as energy balance, consumption of chemicals and generation of enzyme and fermentation inhibitors being paramount for determining its technical and economic viability [4, 8]. Therefore, by choosing the right pretreatment method and by executing it under its optimal conditions, one may meet the basic definition of advanced biorefineries, whereby multiple feedstocks can be converted to several value-added products ranging from fuels, chemicals and materials with wide applications in industry and in the transportation sector.

MAIN PRODUCTS FROM BIOREFINING OF LIGNOCELLULOSIC MATERIALS

According to the National Renewable Energy Laboratory (NREL, USA), biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals [29]. The main driver for the establishment of biorefineries is process sustainability. Hence, this assessment must take into account the food vs. fuel

dilemma, the land-use and water requirement for primary production and the impact on soil fertility, biodiversity and greenhouse gas emissions [7, 29].

Biorefinery has been suggested to provide relevant substitutes to a number of products derived from crude oil. In general, biorefineries can be classified in three different types. Type 1 (or first-generation) has little or no feedstock flexibility and a limited processing capability to produce fuels and co-products. Type 2 (or second-generation) has wider options in end-products but little flexibility in the incoming feedstock. Finally, type 3 (or third-generation) is flexible for both feedstocks and end-products, being able to exploit locally available biomasses to produce a variety of industrially attractive products and/or materials [30]. This advanced biorefining facility could produce one or several low-volume, high-value chemicals and a low-value, high-volume liquid transportation fuel, while generating process heat and electricity for its own use and for selling it to the grid. In this configuration, power production would reduce costs and avoid greenhouse gas emissions, high-value chemicals would enhance profitability and bulk liquid biofuels would feed the market to meet the national energy demand.

Another way of classifying biorefineries may be related to the type of incoming feedstock in a similar way to what has been applied to biofuels. High-value edible feedstocks such as neutral lipids, starch and sucrose are converted by first-generation technologies. Second-generation would apply to the utilization of non-edible lignocellulosic materials including agricultural, agroindustrial and forest residues. Finally, non-conventional feedstocks produced by fermentation processes (yeasts, fungi and microalgae) would characterize third-generation technologies for the production of fuels, chemicals and biomaterials [29, 31, 32]. However, the classification described in the previous paragraph is more consistent as it considers both feedstocks and products to classify different types of biorefinery strategies.

Pretreatment is normally required to assist biomass conversion processes that are associated to the development of type 3 biorefineries. Also, pretreatment is critical for the production of second-generation biofuels such as cellulosic ethanol [1, 6, 10]. Several process streams may be generated by pretreatment and these are tentatively summarized in Table 2. Due to the chemical composition of such feedstocks, products were organized as derived from cellulose, hemicelluloses, lignin, extractives and ashes.

Table 2. Main products directly obtained from pretreatment of lignocellulosics for biorefinery applications.

Fraction	Product	Process
CELLULOSE	Glucose	Acid hydrolysis
	Dissolving pulp	Pulping and bleaching
	Cellulose derivatives	Pulping, bleaching and chemical modification
	Cellulose nanocrystals	Pulping, bleaching and enzymatic hydrolysis
	Cellulose nanofibers	Pulping, bleaching and mechanical refining
HEMICELLULOSE	Monosaccharides	Acid hydrolysis
	Oligosaccharides	Autohydrolysis and mild dilute acid hydrolysis
	Furan compounds	Carbohydrate dehydration
	Hydrocolloids	Partial acid hydrolysis and functionalization
	Liquid fuels	Fermentation after acid hydrolysis
LIGNIN	Phenolic acids	Hydrolysis, acid or alkaline; oxidation
	Vanillin	Oxidation
	Lignosulphonates	Sulphite pulping; SPORL
	Liquid fuels	Pyrolysis, followed by fraction distillation or not Gasification followed by Fischer-Tropsch synthesis
	Solid fuels	Precipitation, drying and densification
	Gaseous fuels	Gasification followed by gas cleaning
	BTX	Pyrolysis followed by fractionation
EXTRACTIVES AND ASHES	Phenolic compounds	
	Organic acids	Supercritical CO ₂ ; solvent extraction; high pressure bleeding
	Food additives	
	Fillers	Calcination
	Catalysts	

Cellulose is a β -(1-4)-D-glucan that yields glucose by complete enzymatic hydrolysis. Acid hydrolysis can also be used for the same purpose but not without releasing 5-(hydroxymethyl)furfural by dehydration and other reaction by-products such as formic and levulinic acids as well as a range of other furan derivatives. Glucose is an easily fermentable sugar that can be converted to biofuels such as ethanol, butanol and hydrogen, as well as organic acids, ketones, higher alcohols, aminoacids, hydrocarbons and several types of biopolymers [33]. Moreover, glucose can be reduced to sorbitol and be catalytically converted to a large variety of chemicals by a wide variety of chemical routes.

Pulping processes are known as the most successful biomass conversion process available to date. Apart from pulps for paper making, other high value-added products can also be produced. For instance, dissolving pulp is a high-quality pulp product containing high cellulose (90%) and low hemicellulose (4%) contents, and trace levels of other biomass-derived components [33]. This product can be used to produce viscose rayon, nanocellulose and cellulose derivatives such as acetate, nitrate and ethers that have broad markets in the fields of textile, military industry, chemical

industry, food, coatings and in material science [34]. The market demand for dissolving pulp is growing steadily in the past few years. For instance, the global production capacity of dissolving pulp was about 8.4 million tons in 2017, and China imported as much as 2.6 million tons [35].

Among the many opportunities arising from biomass conversion processes, cellulose nanomaterials are considered of high economic value and great general interest by several industrial sectors including textiles, food and pulp and paper. These products were classified by TAPPI (Technical Association of the Pulp and Paper Industry, USA), accordingly to proposed standards terms and definitions for cellulose nanomaterial WI3021 [36] in two different categories as (a) cellulose nanofibers (CNF), whose diameters are below 100 nm, and (b) cellulose nanocrystals (CNC), whose diameters and lengths are below 100 nm. In recent years, a greater demand for the development of a biobased economy has contributed to an increase in the investment for the production of nanocellulose materials that are mainly applied in paints as viscosity modifier, in coatings for better stability and homogeneous spreading), in cements as reinforcement agents [37],

in automotive replaceable parts as plastic reinforcement for composites, in paper making to improve mechanical properties [38] and in packaging as barrier to control humidity and gas permeation [39].

Hemicelluloses are less-recalcitrant non-cellulosic heteropolysaccharides that are composed of several building blocks including pentoses, hexoses, uronic acids and acetyl groups [40, 41]. In this category, xylans deserve special attention because they are the most common hemicellulose found in hardwoods and herbaceous crops. As any other plant polysaccharide, xylans can be hydrolysed to monomers (mostly xylose) to produce xylitol by catalytic hydrogenation, furan compounds (mostly furfural) by carbohydrate dehydration, and liquid fuels and many other biobased products by fermentation [40]. Hemicellulose hydrolysates can also be used to produce biopolymers such as poly(lactic acid) and poly(butylene succinate) that are natural substitutes for petrochemical plastics such as polyethylene terephthalate and polybutylene terephthalate [29, 41]. Pretreatment at low severities may convert xylans into xylo-oligosaccharides (XOS) with a direct application in commercially available prebiotics. XOS can be obtained from xylans by partial acid hydrolysis, by enzymatic hydrolysis or by a combination of these [42]. For applications in the food industry, the enzymatic hydrolysis route is preferred because it does not lead to the formation of undesirable side products such as furan compounds and organic acids.

Lignin is the most recalcitrant and the second most abundant biopolymer found on Earth. This polyphenolic macromolecular component is primarily composed of phenylpropane units with varying degrees of methoxylation and its unique availability, properties and composition have been exploited in many ways to compete with and/or replace a wide range of petrochemicals [43]. Lignin can be converted to a variety of commercially valuable chemicals and materials, including hydrocarbons, cinnamic acids, phenols and catechols, benzylic aldehydes, quinones, alkyl benzenes, bio-oil, carbon fibers, activated carbon and polymeric materials such as phenol-formaldehyde resins. The processes used to break down lignin into valuable products are similar to those used in oil refineries, such as pyrolysis, acid and base (alkaline) catalytic systems, and reductive and oxidative processes [44].

A novel and promising field for lignin derivatives is in the construction of light-mass vehicles. Recently studies have demonstrated that

40 to 50% of the steel used in a vehicle could be replaced by lignin-derived carbon fibers [45]. Lignin obtained from lignocellulosic biorefineries could be an ideal precursor for carbon fibers, thereby replacing costly polymeric materials such as poly-acrylonitrile and opening a myriad of other applications in the development of biobased sustainable materials [46]. Despite its tremendous potential for biorefining, about 60% of the lignin produced nowadays primarily by *kraft* pulping is utilized for heat and power to meet the internal energy demand and to facilitate the recovery of chemicals in large scale industrial facilities [47]. However, lignin fractionation and/or depolymerization may lead to the production of several highly functionalized molecules including phenolic aldehydes such as vanillin, syringaldehyde and *p*-hydroxybenzaldehyde, phenolic ketones such as acetovanillone and acetosyringone, phenolic acids such as vanillic and syringic acids and a wide range of other chemicals [48, 49]. For a deeper knowledge about lignin utilization for fuels, chemicals and materials, please refer to some of the most recent reviews in this topic [20, 49-52].

CONCLUSION

The recalcitrance of the plant cell wall macromolecular structure is the ultimate barrier for the development of sustainable biorefineries based on biomass conversion processes. For this reason, pretreatment and fractionation plays an important role in such process development. The first challenge is to select the right pretreatment technology for potentially available biomass sources and then to optimize it in such a way to achieve the best possible yield of a variety of marketable biobased products such as fuels, chemicals and materials.

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