10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

New Generation Urban Biorefinery toward Complete Utilization of Waste Derived Lignocellulosic Biomass for Biofuels and Value-Added Products

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Abstract

Biorefinery is an emerging strategy to progressively replace the conventional refinery. This technique aims to produce biofuels and value-added products from lignocellulosic biomass. With intensive research efforts, a number of innovative technologies have been developed to utilize the building block chemicals from biomass. However, application of the new technique needs to consider the three pillars of sustainable development, *i.e.*, economic, social and environmental development. The concerns could be feedstock- or region-specific, resulting in completely different requirement of desired process under different circumstances. This study reviews the key design concepts and the strengths of the most promising techniques for biomass conversion. Particular attentions are paid to complete utilize all the building block components in the feedstock. Operational parameters such as energy, water, and chemicals are investigated to select desired processes for bioenergy production. The review aims to present the past, current and future research and process development for high efficiency biofuel production.

Keywords: bioenergy, biofuels, biorefinery, lignocellulosic biomass, pretreatment

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1. Introduction

Bioenergy is a valuable resource which has been strategically promoted for mitigating climate changes [1, 2]. Lignocellulosic biomass, the feedstock of bioenergy, is also the only renewable and economical source of valuable bio-products [3]. The non-food based biomass derived from municipal services and agricultural activities are sustainable feedstock for bioenergy production without affecting the food security [4]. Bioenergy has been utilized through the two well-known technical routes in biorefinery, *i.e.*, the thermochemical and sugar platforms processes. Bioconversion process has been selected for less contaminated feedstock due to its moderate processing conditions and outstanding potentials of chemical by-products [5]. Vary significantly among different regions, desirable biorefinery technique may be function specifics and affected by many factors, *i.e.*, types and conditions of biomass, scope of application (*i.e.*, profit-earning or environmental protection), energy price, policies, social background, and availability of infrastructure [6]. There is no universal system to meet all the requirements for bioenergy harvesting.

Bioconversion of biomass includes a series of unit processes, such as pretreatment, saccharification, fermentation, and separation [7]. Design criteria of the unit processes are closely related to the types of biomass. Representative biomass includes wheat straw [8], corn stover [9], sugarcane bagasse [10], rice straw [11], rice husk [12], oil palm empty fruit bunch [13, 14], and forestry residues [15, 16]. Owing to increased attention to solid waste management [17] the feasibility of applying biorefinery to convert wastes derived biomass have also gained wide interests by the community, such as food wastes [18], textile waste [19], woody product (or "timber") waste [20], and yard waste [17, 21]. Biomass can be originated from different parts of the plants, *i.e.*, leaves, braches, bark, stems, and trunk. Each part of the plant consists of different forms and amounts of building block components (*i.e.*, cellulose, hemicelluloses, and lignin) bundled together in a sophisticated 3-D structure [15, 22]. To maximize the yields of the value added chemicals the plant cell wall needs to be well-decomposed before further processing.

Many innovative biorefinery processes have been recently introduced to completely utilize the lignocellulosic chemicals, but most of those reports emphasize only on the achieved yields of the product(s) (*i.e.*, sugars, biofuels, and/or lignin monomers). The critical economic and/or sustainable development factors such as requirement of instruments (*e.g.*, steam explosion system), its operational difficulties (*e.g.*, water and energy consumptions), and potential impacts to the supporting systems have not yet been widely addressed. Therefore, this study investigated the details of the water-biomass-energy nexus among the biorefinery processes. The state-of-the-art techniques were classified into three main groups: (I) lignin fractionation; (II) whole slurry simultaneous saccharification and fermentation (SSF); and (III) one-pot biorefinery. According to the defined category the mechanisms and numerical inputs involved in biomass dissociation are measured or reported and the processability of the easily degradable substrates as well as lignin products are introduced, which further illustrate the benefits of each process. Through the classification and the related solvent-energy based parameters we hope to provide researchers and stakeholders new insights in developing more comprehensive biorefinery systems toward large scale applications.

2. Three Design Concepts of Whole Cell Biorefinery

The reactions occurring in the three types of biorefinery processes for whole biomass utilization has been presented in Fig.1. Plant cell walls were composed of three components, *i.e.*, cellulosic fiber bundles (thin black lines), hemicellulose (thicker green lines), and lignin (thick red lines). Cellulosic fibers are aligned under either amorphous or crystal structures (shaded area). To utilize all the building block chemicals, Type I biorefinery aims to completely dissociate the structural lignin and keep it in the spent liquor. Lignin fractionation can be achieved by alkaline [23], organosolv [24], ionic liquid (IL) [25], and/or deep eutectic solvents (DES) processes [26]. In these processes the majority of hemicelluloses shall remain in the fiber bundles so the structural sugars can be recovered after enzymatic hydrolysis. Solid-liquid separation is mandatory in this biorefinery approach so the dissociated lignin can be harvested for functional application and the remaining solvents/catalysts would not affect bioconversion. Type II biorefinery focuses on complete hemicelluloses removal using acid or other catalysts. Steam explosion, DA and sulfite pretreatment are feasible approaches for whole slurry bioconversion. Those processes are designed to reduce the recalcitrant of lignocellulosic biomass without generating inhibitors to saccharification and fermentation. Dissolved lignin after those processes shall not precipitate onto the substrates when the spent liquor was diluted or after pH adjustment [27]. The pretreated slurry can be used directly in SSF without washing and hence the dissolved sugars in the pretreatment spent liquor can be used by the microorganisms [28]. Lignin is not

removed or removed only partially by physical or chemical modifications. This process allows enzyme to access the cellulose through the inner surface for hydrolysis and therefore result in high substrate digestibility after enzymatic hydrolysis. While enzymatic hydrolysis may be difficult if too much chemical reagents or lignin are remaining in the substrate [23]. Finally, Type III biorefinery is developed to decompose both lignin and hemicelluloses for functional applications. Cellulose shall become easily hydrolysable after swelling, or regeneration with or without solid-liquid separation and/or washing. Many ionic liquids (ILs), *i.e.*, 1-ethyl-3-methylimidazolium acetate ([C$_2$mim][OAc] or [Emim][Ac]) can effectively dissociate lignin and hemicelluloses [29, 30], as well as reduce the crystallinity of cellulose [31]. In this process, the dissociated lignin and hemicelluloses can be withdrawn from the cellulose-rich substrate [32]. The de-crystallized substrate can be regenerated after washing and become easily accessible by cellulase. The only concern of IL pretreatment processes is the high complexity of the multi-scale processes and the negative impacts of residual IL or grafting of functional groups on cellulose to affect enzyme activity. To overcome this problem, Shi et al. [33] developed an innovative strategy to simultaneously extract the fermentable sugars, recover lignin, and recycle the IL in one pot and successfully harvested 81.2% glucose and 87.4% xylose in 72 h.
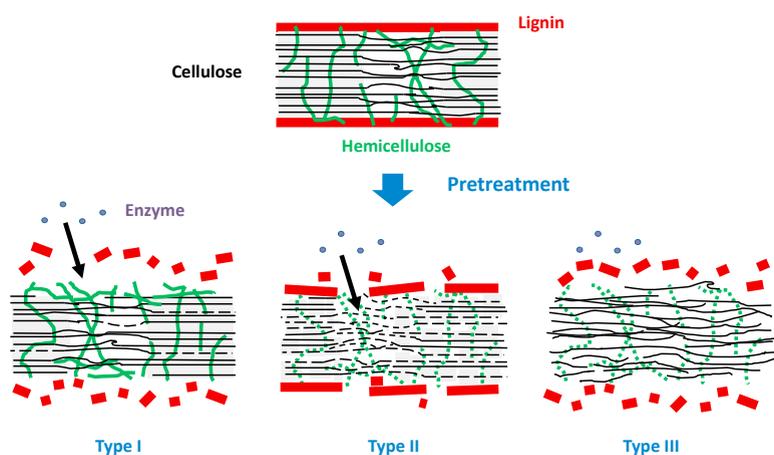

Figure. 1. Three types of plant cell wall decompositions in major biorefinery processes

3. Valorization of Building Block Chemicals

New generation biorefinery have broadened its focus of feedstock from rapidly degradable sugars/starch (food crops), cellulosic fibers (mainly for paper making) and then to aromatic compounds (such as lignin monomers and value-added products) [34]. New values of the building block components have been discovered as well as new challenges toward large scale applications. The fundamental concepts and economic indexes (*i.e.*, product yields and market values) of selected products and building block chemicals harvested from modern pulp mills or biorefinery for future studies have been provided in Table 1.

Table 1. Approximate prices of selected chemicals from hardwood [35]

Chemicals	Market price (USD/kg)	Maximum yield (%)
Pulp	0.3-0.9	40-50
Glucose	0.4-0.5	40-45
Xylose	1.0-5.0	20-30
Crude lignin	0.1-0.3	54-75
Lignin monomer	6,000-12,000	6-38

3.1. Carbohydrates

Cellulose and hemicelluloses are covalent bonded long-chain biopolymers. Simple solvent treatment can conditionally loosen the polysaccharide structures (*e.g.*, glucan or xylan), but cannot completely hydrolyse cellulose

without appropriate catalysts (such as acid) or high temperature. Enzymatic hydrolysis is currently the most widely applied approach to harvest the fermentable sugars. The mechanisms of the interactions between dissociated and residue components to enzyme activities are biomass-specific and as a function of pretreatment severities [22]. Some images of the pretreated substrates before and after enzymatic hydrolysis were provided in Fig.2(a) to Fig.2(d). The surface of woody biomass before pretreatment (Fig.2 (a)) was smooth with the inner surface well protected from hydrolysis. Organosolv (ethanol), alkaline, and SPORL pretreatment opened up the plant cell wall (red arrow) and created different levels of dissociation (from Fig.2(b) to Fig.2(d), respectively). With increased pretreatment severity and lignin removal the damages in cell wall structure and lignin precipitation on the substrate surface gradually become observable (Fig.2(d)). The cell wall structure was decomposed after hydrolysis, while enzyme may be captured under scanning electron microscope (SEM) within 24 hour of hydrolysis (arrow mark in Fig.2(e)). The cell wall can be completely decomposed after enzymatic hydrolysis (Fig.2(f)). Among the three biorefinery processes, the cellulose enriched substrate derived from Type I and Type III biorefinery need to be washed or regenerated before used in the enzymatic hydrolysis process. However, even after sophisticated washing, chemical interferences still exist to affect the digestibility of the substrates [15].
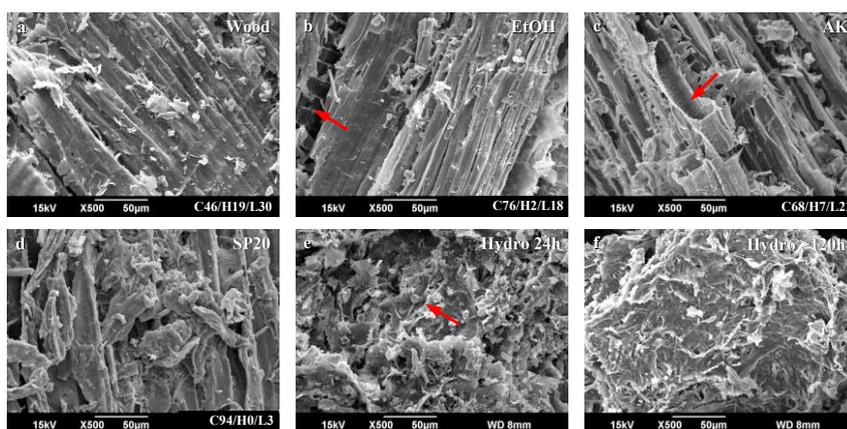

Fig.2 Scanning electron microscopic pictures of Monterey pine wood before pretreatment (a); after organosolv (ethanol) pretreatment (b); alkaline pretreated (no Na$_2$S) (c); sulfite pretreated (low pH) (d); within 24 h after enzymatic hydrolysis (e); and 3 months after enzymatic hydrolysis (numerical symbols after C/H/L shows the chemical composition of the cellulose/hemicellulose/lignin contents) (f).

3.2. Lignin

Dissolved lignin has been used to produce lignin monomers after direct hydrogenolysis but the yields of hydrogenolysis were largely dependent on the quality of lignin. The yield of conversion for solid untreated biomass was 45-55 mol.%, while the conversion of organosolv pretreated lignin decreased significantly to 5-20 mol.% [36, 37]. The reduction of yield is mostly due to lignin condensation during the pretreatment process. The results of 2D HSQC NMR spectra suggested that lignin structure obtained after GVL pretreatment was similar to native lignin, which could be attributed to the low extraction temperatures achievable using GVL solvent [38]. The theoretical yields of monomer were still below 70% from GVL pretreated corn stover and below 40% for maple wood, indicating that lignin condensation occurred during the thermochemical process. Luo et al. [39] compared three organosolv (*i.e.*, methanol, acetone, and acetic acid) for extraction of native lignin from wild-type and genetically modified poplars. Methanol extracted lignin gave the best yield of >60% of aromatic products (*i.e.*, guaiacol, isoeugenol, and 4-propenyl syringol). NMR spectroscopy demonstrated that methanol served as a nucleophile reacted with the Cα benzylic carbocation formed during the organosolv pretreatment while minimizing lignin condensation during the pretreatment process. Shuai et al. [37] added formaldehyde during biomass pretreatment and produced a soluble lignin fraction that can be converted to guaiacyl and syringyl monomers at near theoretical yields during subsequent hydrogenolysis (47 mole % of Klason lignin for beech and 78 mole % for a high-syringyl transgenic poplar). These yields were three to seven times higher than those obtained without formaldehyde, as lignin condensation was prevented by forming 1, 3-dioxane structures with lignin side-chain hydroxyl groups.

4. Sustainability concerns of biorefinery

Bioconversion is an environmentally attractive option to valorize biomass derived from organic wastes. Biorefinery, in comparing with incineration or pyrolysis, can better preserve the valuable components in the plant cells for functional utilization. With large amount of new findings, it is foreseeable that the related techniques could be commercialized in the next decades. The related environment and technical concerns, however, has not been categorized or widely disclosed in most of the literatures, which most likely owes to lack of information of different processes. Meanwhile, biorefinery is a multi-staged process including many different processes in a broad range of technical discipline, *i.e.*, plant science, thermochemical systems, and biological processes. Selection of techniques for different applications needs to consider the region- and technique-specific limitations, such as industrial background, supportive experts, and infrastructures. This chapter summarizes the environmental and technical criteria of three basic biorefinery concepts toward sustainable development of biomass valorization.

4.1. Phases of reagents

Environmental issues of biorefinery system may be referred to direct contamination or in-direct impacts due to excessive waste of resources. Direct environmental impacts such as effluent toxicity to fish or emissions of volatile organic compounds (VOCs) can be directly monitored by instruments and the acceptable values have been well-regulated by the stakeholders. Indirect environmental measures such as reactor profiles, risks of operation, and water footprints are more relevant to process design/control conditions and are more difficult to regulate. Elevated operation pressure induced by the applied chemicals at the desirable temperature is a critical parameter affecting the reactor profile, operation difficulty, and capital costs of the biorefinery. Fig. 3 shows the phase diagrams of typical solvents used in the pretreatment processes (curves) and the representative ranges of operation temperatures (symbols) based upon published works. The optimal operation pressures of different pretreatment processes ranged dramatically from approximately 10 kPa (GVL) to nearly 10,000 kPa (ammonia) at 120°C. The vapor pressure of the reagent solvent increases nearly exponentially with increased operation temperature in the confined space. Typical autoclaves operating are designed to hold 100-110 kPa, which is approximately equivalent to the pressure of water vapor operating at 100-121°C, respectively. Other low-boiling point solvents such as THF or ethanol require special high-profile reactor to hold at least 1-1.2 MPa pressure at temperature between 150-210°C. This requirement limits the applicability under various conditions or region.
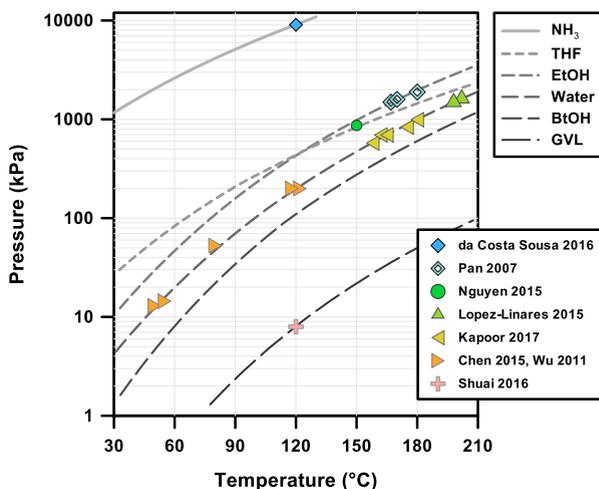

Fig.3 Temperature-pressure relationships (curves) of different solvents for biomass pretreatment. Symbols represent the practical ranges of pretreatment temperatures used in published studies. Note: the pressures were presented in log scale.

4.2. Energy-water nexus

The effectiveness of plant cell wall dissociation is roughly related to the liquid/solid (L/S) ratios during the thermochemical pretreatment process. The average L/S ratios of representative pretreatment processes were demonstrated in Fig. 4. The liquid portion is contributed by water and co-solvents (e.g., the organosolv processes) and the error bars showed the standard deviations of different processes. With increased cooking temperatures the L/S ratios were gradually reduced for withdrawing similar amounts of cellulose (80%) from the feedstock in the studies. Meanwhile, the residue lignin contents also decreased with increasing temperature (results not showed), which may be due to the reduced severity of chemical reagents/co-solvent(s) used in the processes. The broadest ranges of L/S ratios and cooking temperature were observed for the alkaline pretreatment. Organosolv processes cover a wide temperature ranges but not the L/S ratio. Dilute acid and SPORL pretreatment can be conducted at different temperature with wide variety while water vapor based steam explosion can be only conducted at high temperature (>200°C). Biorefinery energy is directly related to the amount of liquids (solvent + water) used in the pretreatment and SSF processes [28]. When more water was used in the pretreatment and fermentation processes, more energy was needed in the cooking and distillation processes (more detailed calculation of the water-energy nexus please referred to Dong et al., [28]). Alkaline pretreatment processes used larger amount of water (12.8 w/w for cooking, and 9.7 w/w for washing/fermentation water) than other processes, which may be due to its capability in delignification at lower cooking temperatures. SPORL and one-pot IL biorefinery required less amount of water (3.7-4.0 w/w for cooking and 4.4-6.2 w/w for washing and fermentation water), but it use smaller amount of fermentation water. It should be also noted that the numbers reported here were just to reflect the current status of recently published works with promising performances. It does not represent the final capacities for full-scale applications. It showed the possible directions for future development while it should not be used for making any conclusive comparison. Meanwhile, all the washing processes were assumed to be accomplishable by using three times of rinsing waters for one unit mass of pretreated biomass (in dried weight) and the solid loads of effective SSF were all at 15 wt.% disregarding the small variations among different publications.
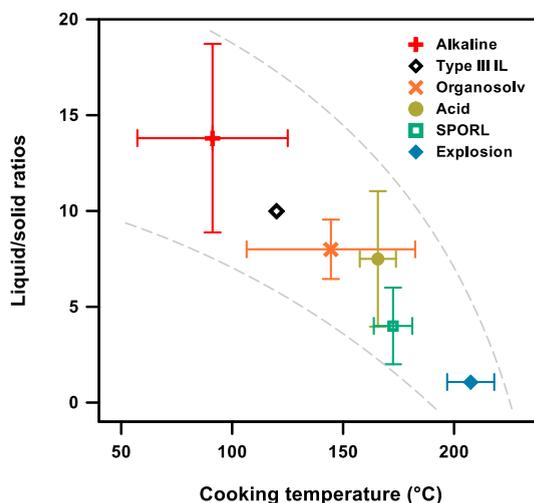

Fig.4 Liquid/solid ratios of published pretreatment processes as a function of treatment temperature. Water (with co-solvent) consumption reduced with increased temperature.

5. Visions and future development

Applying biorefinery for waste valorization is a prospective way to mitigate climate changes without damaging food security. The three biorefinery strategies reviewed in this study all aim to maximize the benefits of bioconversion processes but limitations still existed to be resolved. Type I biorefinery is a relatively mature process

(*e.g.*, Kraft pulp) that can produce high quality lignin and cellulose; but it is energy intensive and may not completely harvest the hemicelluloses for fermentation. Type II biorefinery can produce highest titer of fermentation products; but its lignin by-products are with lower values and may create more negative impacts to the environment. Finally, Type III biorefinery is with high potential and, without the need of high profile digesters, very simple to operate; but the IL can be very costly and difficult to recycle. Meanwhile, water consumption of the related processes should not be overlooked as it is closely related to energy consumption, reagent recyclability, product yields, and environmental problems. The parameters provided in this review addressed the difficulty of biorefinery and should be optimized with proper experiments before region-wide applications.

Acknowledgements

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