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Hydro-Fractionation for Biomass Upgrading

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Abstract

Lignocellulosic biomass is mainly composed of three components including cellulose, hemicellulose, and lignin. A fractionation step is considered as one of the most important preliminary processes for the separation of these three components before their further utilization. Among different separation techniques, water-based pretreatments or hydro-fractionations including (a) subcritical water extraction, (b) supercritical water extraction, and (c) steam explosion have shown their promising advantages both in terms of separation efficiency and in terms of environmental friendliness. Several hydro-fractionation technologies have been developed during the last decade in which each fractionation process has different impacts on the compositional and structural features of biomass. The fractionation principle, current status, and their potential uses in the biorefinery for sugar-based chemical platform production are mainly discussed.

Keywords: lignocellulosic biomass, hydro-fractionation, subcritical water extraction, supercritical water extraction, steam explosion, bio-based product

1. Introduction

The fossil fuel demand from industrialization and domestic utilization has been continually rising, which is in contrast to the depleting supply of petroleum resources that leads to public concerns for the adequacy of long-term energy supply and also environmental issues due to greenhouse gases being drastically released. In addition, the expanding consumption of natural resources also drives the global community to force with economic problems. The replacement of supplies from fossil fuels, which is one of the challenging tasks, has been of intense concern. The use of alternative energy from renewable resources is a promising solution not only for long-term environment sustainability but also in economic aspects. Plant biomass including agricultural, forestry, herbaceous,

and residue, which is a sufficiently abundant natural renewable resource, has been considered as a suitable alternative carbon source that can be converted into useful sustainable products and varieties of chemicals. Among these, the exploitation and utilization of biomass energy have motivated and attracted a great deal of interest from around the world due to a power opportunity to improve energy security, reduce the trade deficit, dramatically lower greenhouse gas emissions, and improve price stability [1]. Besides the advantages mentioned above, agricultural biomass such as crop residues are generated with large quantity annually, making them promising sources for further utilization due to their abundance, diversity, and low-cost. Therefore these potential biomass residues can play important roles as sustainable carbon sources.

The term “lignocellulosic agricultural residues” is used for describing all organic materials which are produced as by-products from harvesting and processing agricultural crops. Chemically, lignocellulosic agricultural residue can be generally regarded as being composed of three polymers including 40–50% of cellulose, which is a major component, 25–30% of hemicellulose, and 15–20% of lignin along with smaller amounts of pectin, protein, nitrogen compounds, and inorganic ingredients [1]. Crystalline and amorphous bundles of cellulose form a skeleton surrounded by the covalently linked matrix of hemicellulose and lignin [2]. These polymers are associated with each other in a hetero-matrix and varying relative compositions depending on the system, type, species, age, stage of growth, and even source of biomass, and they can be in the form of liquids, slurries, or solids. **Figure 1** displays three main components of lignocellulosic biomass.

According to **Figure 1**, each component of lignocellulosic biomass is described below.

Cellulose: the most enormously bountiful biopolymer in the world and the main source of the C6 sugar unit is a linear homo-polysaccharide of D-glucose linked together by β -(1, 4) glycosidic linkages, with cellobiose as the smallest repetitive unit. The long cellulose chains linked together with β -(1, 4) orientation results in the formation of intermolecular and intramolecular hydrogen and van der Waals bonds, which cause cellulose to be packed into microfibrils; they are fine structures bundled up together to form cellulose fibers with highly crystalline structure causing its stable properties, insoluble in water unless at high temperatures or with the presence of a catalyst, and are resistant to enzyme attacks [1, 3].

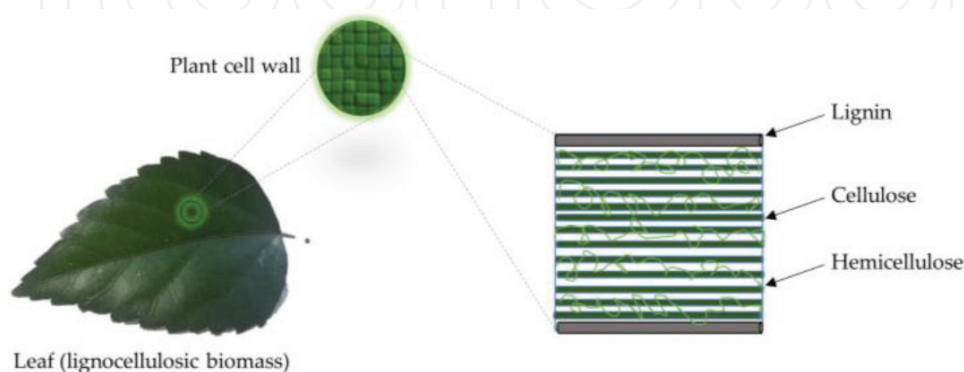


Figure 1. Lignocellulosic biomass composed of cellulose, hemicellulose, and lignin.

Hemicellulose: the second most abundant polymer is a complex, random, and amorphous branched carbohydrate comprising of different polysaccharides, including hexoses (D-glucose, D-mannose, D-galactose), pentoses (L-arabinose, D-xylose), and uronic acid with 50–200 units. The backbone of hemicellulose is either a homopolymer or a heteropolymer with short branches linked by β -(1, 4) glycosidic linkage or β -(1, 3) glycosidic linkage and groups of acetates were randomly attached with ester linkages to the hydroxyl groups of the sugar rings [3]. Hemicellulose has a lower molecular weight when compared to cellulose. Moreover, hemicellulose has short lateral chains, which provide linkage between cellulose and lignin, making hemicellulose easier to hydrolyze and degrade into monosaccharides than cellulose [4]. This allows hemicellulose to be removed under mild reaction conditions.

Lignin: it is a complex hydrophobic, large molecular structure containing cross-linked heteropolymers of three different main phenolic components which are trans-p-coumaryl alcohol, trans-coniferyl alcohol, and trans-sinapyl alcohol, which shield the polysaccharide fibers from external environment stress, microbial attacks, and oxidative stress. Lignin is recognized as the cellular glue and encrusting material due to the existence of strong carbon—carbon bond connection (C—C) and ether linkages (C—O—C), which together provide compressive strength to different compositions and individual fibers of lignocellulosic biomass (**Figure 2**).

The high crystallization region, high degree of polymerization, different connection forces between each composition, the protection effect from hemicellulose, and lignin of the lignocellulosic agricultural residue cell wall are stable and make it hard to be degraded for utilization in a further step; therefore, to convert lignocellulosic agricultural residue to biofuels, energy, or chemical platforms, a large number of pretreatment approaches have been investigated on a wide variety of feedstocks to deconstruct and fractionate the complex network structure to its simpler molecules in order to increase the efficiency of biomass composition utilization. Several fractionation technologies have been developed during the last decades. Those methods are usually classified into physical, biological, chemical, and physicochemical pretreatments. The several key properties to take into consideration for low-cost and advanced pretreatment processes are (a) the large amount of yield and harvesting time of feedstock, (b) the large volume of accessible pretreated substrate, (c) less sugar degradation, (d) a minimum number of inhibitors generated after the reaction, (e) a reasonable size and cost of reactor, (f) less solid waste production, (g) effectiveness at low moisture content, and (h) the minimum heat and power requirement [5].

Considering the concerns above, the most cost-effective processes in the biomass upgrading in the industry utilize the dispensable pretreatment and fractionation process where water most

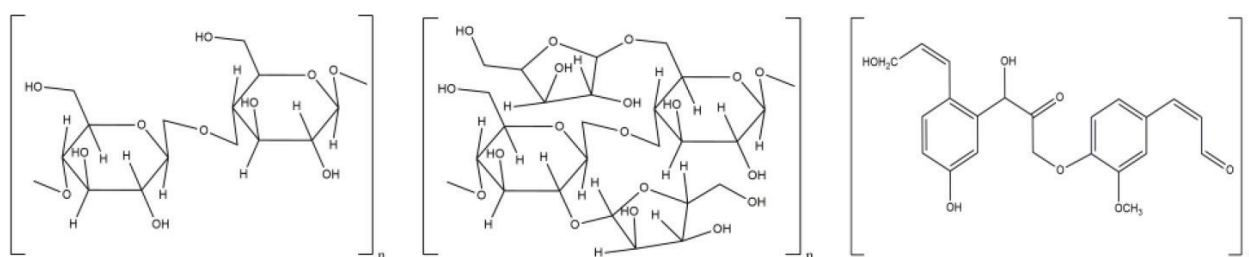


Figure 2. Examples of cellulose (left) hemicellulose (middle) and lignin (right) structures.

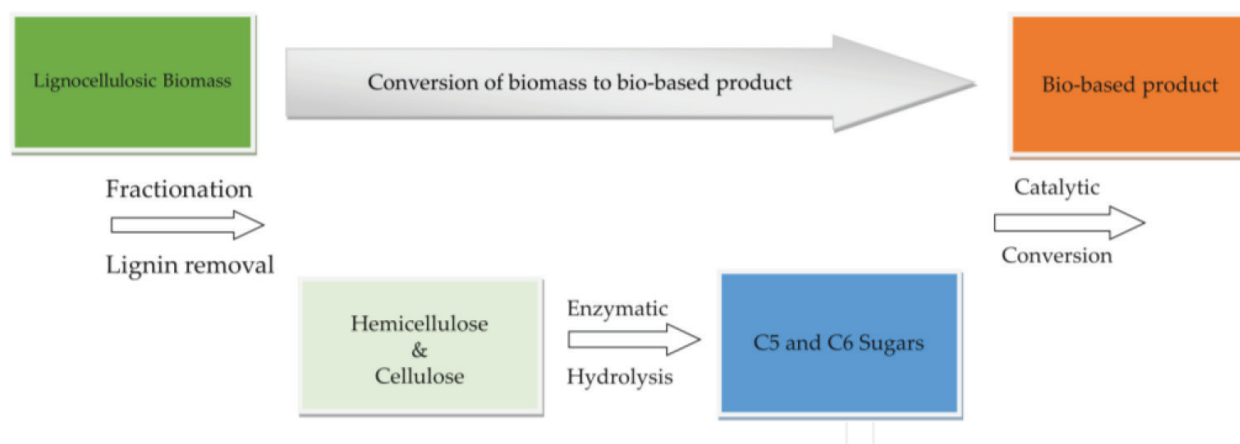


Figure 3. Process for sugar-based chemical platform production from biomass.

certainly takes great effects. The essential function of water in common fractionation includes the following: (a) it acts as a mass transfer medium, (b) it plays as a reactant constructing a mild acidic state due to the mitigation of pK_w at an increased temperature, (c) it performs as a heat transfer medium, and (d) it represents as an explosion medium for explosion pretreatment to tear biomass into small pieces. Due to the advantages of water-lignocellulose interaction and efficacy, many attempts have practically focused on applying water into the fractionation process to separate the mixture of lignocellulosic biomass into an individual composition called aqueous fractionation, hydro-based fractionation, or “hydro-fractionation.” The overall process of bio-based product production from lignocellulosic biomass is shown in **Figure 3**.

Hydro-fractionations or the processes utilizing water as a medium, reactant, or catalyst for separating mixture compositions including subcritical extraction, supercritical extraction, and steam explosion are mainly discussed in terms of their fractionation principle, current status and potential uses, life cycle and bioeconomy.

2. Principle of hydro-fractionation

2.1. Subcritical and supercritical water extraction

Subcritical and supercritical water extractions have been employed extensively in biomass utilization due to the tunable physical and chemical properties of water, potentially valuable products, and environmental friendliness. Furthermore, these two fractionation methods are known as the promising methods to make the biorefinery concept more practical with sufficient and sustainable profit.

Typically, subcritical water is defined as the use of water at a temperature between the boiling point and critical temperature (373–647 K) under pressure, which is high enough to maintain its liquid state. Supercritical water occurs at a temperature and pressure higher than its critical point (22.1 MPa and 647 K). In the supercritical region, the properties of liquid and vapor fuse [6, 7]. The behavior of subcritical and supercritical water near critical point mainly depends on pressure and temperature; therefore, some important properties of water could be tuned

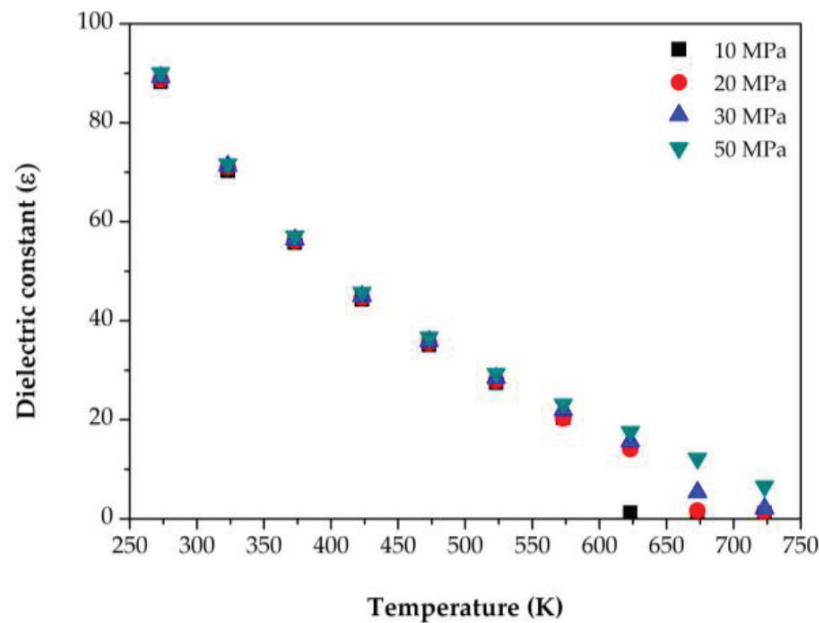


Figure 4. Static dielectric constant of water at various temperatures and pressures [14].

by varying the temperature and pressure for particular conditions of biomass fractionation. In this section, the important properties of water at the subcritical and supercritical state related to biomass fractionation including dielectric constant, ionization constant, density, and viscosity are demonstrated and discussed. A better understanding of water properties under various temperatures and pressures can allow an appropriate experimental design and suitable operating conditions for some specific proposes.

Dielectric constant is a dimensionless value showing the relative permittivity of a material compared with the permittivity of free space. Typically, the high dielectric constant of a solvent means that it has high polarity and vice versa. **Figure 4** shows the influence of temperature and pressure on the dielectric constant. The value of the dielectric constant tends to decrease with the increasing temperatures while it is slightly affected by pressure around the critical point. This phenomenon hints that the polarity of water can be reduced by increasing the temperature which indicated that the solubility of hydrophobic organic compounds and low molecular biopolymers in biomass could be enhanced by using low polarity of water generated at elevated temperatures [8–10]. It is worth mentioning that low polarity of water also reduces the solubility of salt in the process, especially type 2 salts (classified by solubility behavior) such as Na_2SO_4 , Na_2CO_3 , and K_2SO_4 [11], and the participation of salt might cause fouling that diminishes the efficiency of the process or even terminates the process. Therefore, the water supply should be treated to eliminate type 2 salts before its use in the process; also, a special design of a reactor might be required in case of raw material containing high contents of type 2 salts [12, 13].

The ionization constant of water is the ratio between the concentration of ionic ($[\text{H}_3\text{O}]^+$ and $[\text{OH}]^-$) products and the reactant at the equilibrium condition. The influence of temperature and pressure on the ionization constant is shown in **Figure 5**. In the subcritical region, the ionization constant increases with the raising of temperature and is slightly affected by the increase of pressure. On the other hand, beyond critical temperature, the ionic constant

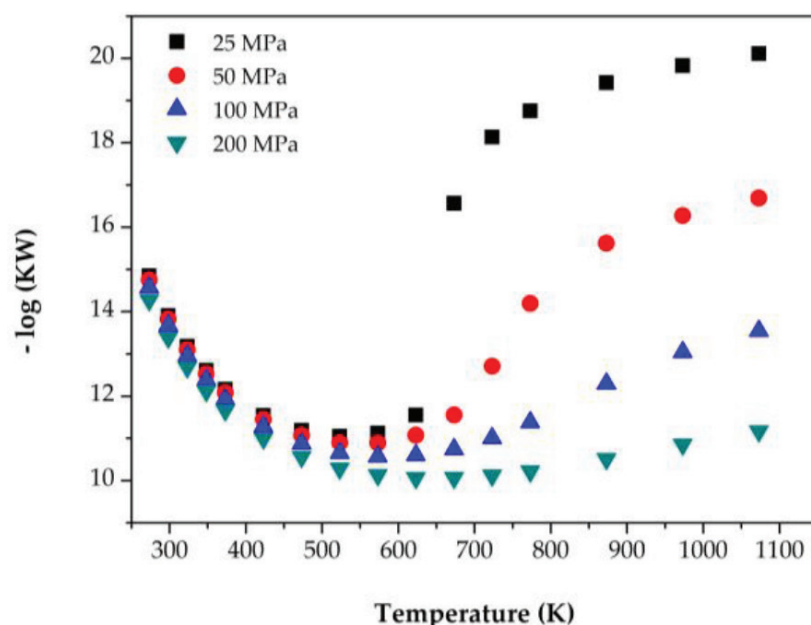


Figure 5. Negative log (base 10) of ionization constant of water at various temperatures and pressures [19].

declines with the increase of reaction temperature and dramatically drops with the reduction of pressure. Therefore, the reaction of biomass degradation takes place in ionic media for subcritical water extraction. On the other hand, the supercritical water extraction provided a radical-oriented environment for biomass fractionation [15–18].

Density of water is defined as the ratio between the mass and volume of water at a specific temperature and pressure. The density of water is decreased with the increase of temperature due to the expansion of the volume. With the increase of pressure, the density of water increases. The higher density of water at specific conditions provides a better chance to penetrate the biomass structure [20].

The viscosity of water is the resistance of water from the external stress such as tensile strength and shear strength. It refers to the resistivity of the water over movement or deformity. The viscosity of water decreased with the increase of temperature but only a slight change was observed when the pressure increased in the subcritical region. However, a more effect of higher pressure was found in the supercritical region on the higher value of viscosity. The viscosity has a direct effect on biomass fractionation. Since the small value of water viscosity provides better wettability of the biomass, the penetration of water to destroy the biomass structure increases (**Figure 6**).

2.2. Steam explosion

Steam explosion, one of the most widely employed hydrothermal technologies for pretreating lignocellulose in industrial applications to convert biomass into useful chemicals, has been recognized as an environmental friendly pretreatment method that can effectively enhance subsequent enzymatic hydrolysis without the necessity of using chemicals, except water, which can lower environmental impact, lower capital investment, bring more potential for energy efficiency, and give rise to less hazardous process chemicals and conditions; this offers several attractive features when compared to hydrolytic acid and oxidative processes. Steam explosion involves exposing wet lignocellulosic biomass to high-pressure saturated steam (0.69–4.83 MPa) and temperature

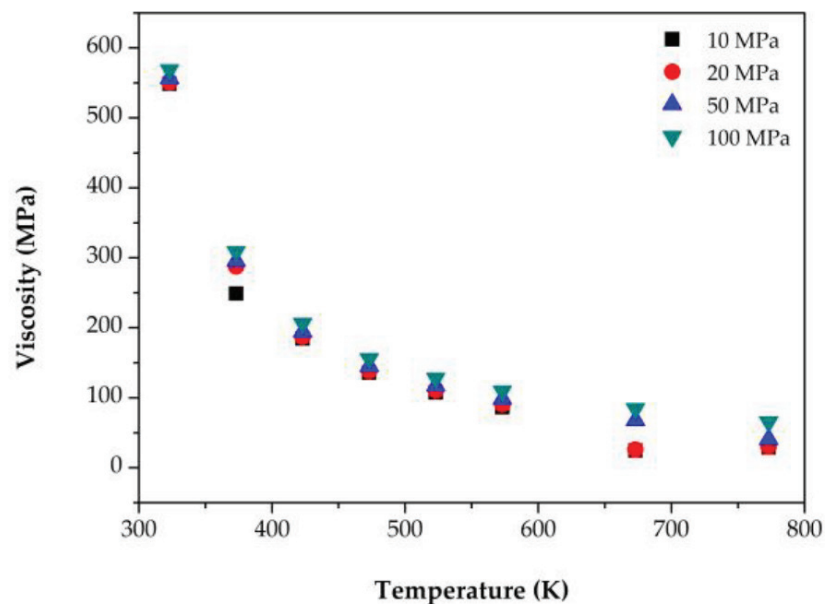


Figure 6. Viscosity of water at various temperatures and pressures [21].

(433–533 K) for a period ranging from seconds to several minutes and then suddenly depressurizing it to atmospheric pressure, making the biomass undergo an explosive decompression. This pretreatment is the combination of mechanical forces and chemical effects due to autohydrolysis of the acetyl group in hemicellulose. Autohydrolysis takes place from the formation of acetic acid from the acetyl group in the hemicellulose structure at high temperature where water acts as an acid at high temperature. The hemicellulose and lignin bonds are cleaved during the explosion, allowing the hemicellulose become water soluble; water-soluble lignin from plant cell wall is also released from the cleavage action into water phase. The mechanical effect is caused by explosive decompression that occurred from suddenly dropped pressure at the termination of the pretreatment, which induced the cell walls in biomass to undergo structural disruption and expansion. Because of these effects, a part of hemicellulose hydrolyzed and solubilized; lignin was redistributed, lignocellulosic matrix polymer was broken down, particle size was decreased, the degree of polymerization was reduced, and porosity was increased; moreover, cellulose was slightly depolymerized, which led to the improvement of lignocellulose digestibility [22–24].

Supercritical extraction in terms of operating conditions, reaction mechanism, and preferred biomass is shown in **Table 1**.

Hydro-fractionation method	Temperature range (K)	Pressure range (MPa)	Fractionation route	Application
Subcritical water extraction	373–647	>0.001 (maintain liquid phase)	Liquid ionic reaction	Extract desired product
Supercritical water extraction	>647	>22.1	Radical reaction	Extract desired product
Steam explosion	433–533	0.69–4.83	Rapid volume expansion of water	Reduce crystallinity of biopolymer

Table 1. Comparison of different hydro-fractionation methods.

3. Current status of hydro-fractionation

3.1. Patent filing of hydro-fractionation technologies

In **Figure 7**, it showed that numbers of filed patents in fields of subcritical and supercritical water extraction and steam explosion technologies have increased from 2007 to 2015. The trend of patent filing of subcritical water extraction decreased in 2016 and was the same number until 2017. On the other hand, more patents were filed in supercritical water extraction and steam explosion after 2015. Quantitatively, it can be seen that the number of filed patents for supercritical water extraction is a lot greater than that of steam explosion and subcritical water extraction. This could be explained by the fact that supercritical water extraction has more versatile applications than the other two technologies. Since this method is not only employed in biomass fractionation, it could be used in coal, oil, polymer, organic and inorganic compounds, nanomaterial, and waste-recycle applications [25].

3.2. Subcritical and supercritical water extraction

With the adjustable properties of water regarding operating temperatures and pressures described earlier, subcritical and supercritical water extraction were applied in many studies to resolve the complexity of the biomass structure. To achieve the maximum benefit from the utilization of biomass in the biorefinery, the conditions of the selective pretreatment of subcritical and supercritical water extraction were tuned. Therefore, several kinetics of selective products

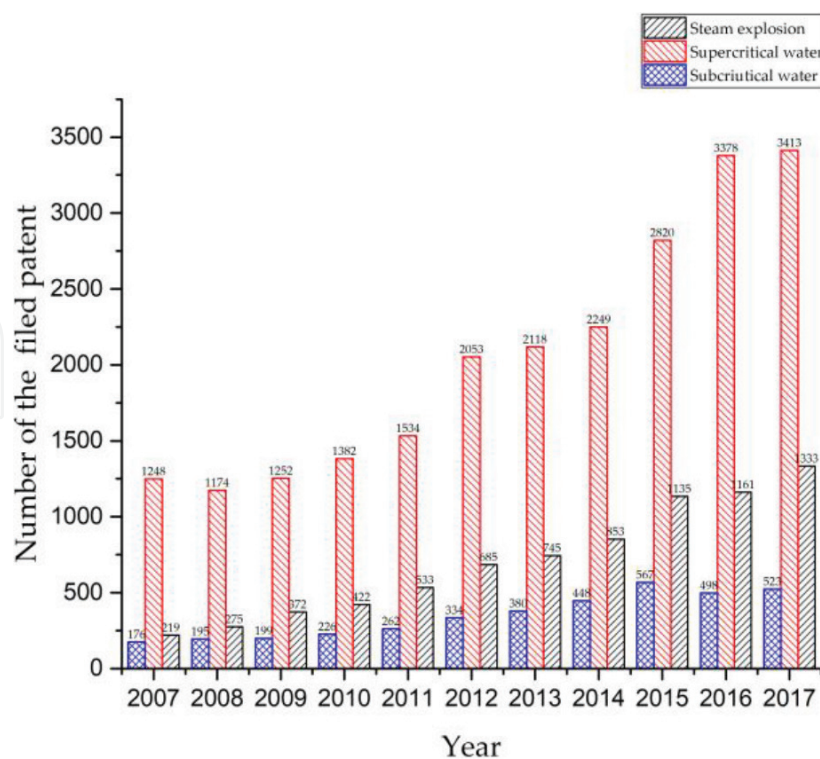


Figure 7. Numbers of filed patents in hydro-fractionation technology.

from the model compounds and the fine conditions including temperature, pressure, heating rate, and residence time were published [26–29]. It is worth mentioning that in subcritical extraction, temperature, heating rate, and residue time enormously affected the reaction behavior and desired products, while the role of pressure is to maintain water in a liquid state and increases the rate of reaction. On the other hand, the effect of pressure on the reaction and kinetics was gained at the supercritical water state [30]. The first component after the degradation of biomass under hot compressed water is hemicellulose at a temperature above 453 K. Typically, at a suitable temperature, a random cleavage between monomeric sugar bonds took place and hemicellulose oligomers were extracted when the chain was cleaved until shorter chains were obtained. And if the reaction time is high enough, another reaction called deacetylation occurred and gave acetic acid. With higher temperature, the product yield was increased but the selectivity dropped [31, 32]. Moreover, if the temperature was raised above 513 K, the oligomer of cellulose from the amorphous part in cellulose was generated, leading to the reduction of the solid yield [33]. After the temperature reached 553 K, the products derived from the hydrolysis reaction of cellulose were 5-hydroxymethylfurfural, levulinic acid, formic acid, and lactic acid [34–36]. For the extraction of lignin, there was a handful of evidence that indicated that the decomposition temperature of lignin without the addition of a catalyst was above 623 K and provided phenols, cresols, guaiacol, catechol, and methyl dehydroabietate as its degrading products [37, 38].

3.3. Steam explosion

The steam explosion process offers several attractive features for biomass fractionation technologies. Obviously, this process has low environmental impacts and mild operating reaction conditions, no chemical is required except water, and moist biomass can be used as feedstock; the higher the moisture content, the longer the steam pretreatment time [39]; it provides high sugar yield and small amounts of by-products and offers low capital investment. However, some unwanted degradation compounds occur when the operating condition is excessive (high temperature and pressure). For example, xylose obtained from hemicellulose could be degraded to furfural, and glucose obtained from cellulose could be degraded to 5-hydroxymethyl furfural, respectively. These two by-products are undesirable compounds since they could inhibit some microbial activities. Therefore, some detoxification methods should be determined prior to enzymatic hydrolysis. During the process, heat transfer can generate the issue of overcooking at the surface of the larger biomass particles and an incomplete pretreatment of the interior region [39], so optimization size of the feedstock is also a crucial step to achieve high sugar conversion and low production cost.

Steam explosion can be performed as a process either in a batch or as a continuous reaction with the most important operational conditions as residence time, temperature, and particle size; a combination effect of these parameters that depend upon feedstocks has been operational for steam explosion such as *Salix* [40], orange peel [41], wheat straw [42] and barley straw [39]. In recent years, there have been a good number of researchers who gained interest in the underlying work of water responsibility. Boluda-Aguilar et al. studied the steam explosion pretreatment of lemon (*Citrus limon* L.) citrus peel wastes to obtain bioethanol, galacturonic acid, and other coproducts [43]. The steam explosion pretreatment showed an interesting effect on lemon peel wastes for obtaining ethanol and galacturonic acid. The simultaneous saccharification and fermentation (SSF) processing of steam-exploded lemon citrus peel wastes with low enzymatic

concentration produced more than 60 L ethanol/1000 kg of fresh lemon citrus peel wastes. In addition, it has been discussed that the minimum inhibitory concentration of lemon citrus essential oils on yeast is lower than that obtained from orange and mandarin citrus essential oils. Singh et al. [44] reported the steam explosion of sugarcane bagasse, which eventually showed the enzymatic hydrolysis efficiency of 100% after 24 h of incubation by using the cellulases from *Penicillium pinophilum* with an enzyme loading of 10 FPU/g. To compare its potential use with commercially available cellulose (Accellerase™ 1000), the results indicated that using *Penicillium* cellulase and Accellerase™ 1000 showed that the saccharification potentials are comparable to the treated substrates such as steam-exploded sugarcane bagasse and ball-milled cellulose powder.

In our recent report on sugar production from sugarcane bagasse, the batch-type steam explosion system was developed for lignin removal to increase sugar yield. The sugarcane bagasse was first impregnated in a diluted alkaline solution and subjected to the steam explosion experiment at the temperature range of 433–493 K with the pressure below 2 MPa for a maximum reaction time of 10 min. The study showed good synergy on the combination of diluted alkaline impregnation and steam explosion for enhancing the purity of obtained bagasse leading to the higher yield of sugar production after the enzymatic hydrolysis process [45]. This could be a good evidence to show that the combination of the steam explosion technique and diluted base solution treatment could fractionate the lignin content into the water phase and provide the nonsoluble solid product of cellulose and hemicellulose for sugar production.

4. Life cycle assessment and bioeconomy of biomass upgrading

4.1. Life cycle of biomass hydro-fractionation

For the conversion of the lignocellulosic biomass feedstock to bio-based products, there are several processes involved. Firstly, the agricultural plants are grown and harvested in which the agricultural residues and wastes could then be collected and transported for storage. The pretreatment and fractionation of the biomass are performed to prepare the material for some particular manufacturing processes. The obtained bio-based products are later on distributed to marketplaces and delivered to customers. The life cycle assessment (LCA) is known as a systematic method for evaluating the environmental impact of a product's entire life, starting from growing its feedstock to its disposal process [46]. For example, in case of the bio-based product, lignocellulosic biomass feedstock was generated from agricultural crops which require soil, fertilizers, water, and sunlight for its growth, while water, electricity, and heat are necessary for its manufacturing process. However, to make this chapter concise, only the pretreatment and fractionation process of the feedstock is emphasized.

In a study, Prasad and his team evaluated the life cycle of four different pretreatment methods including liquid hot water (or subcritical) extraction, organosolve extraction, dilute acid extraction, and steam explosion of milled corn stover [47]. The four environmental impacts in terms of climate change, eutrophication, water depletion, and acidification potential were predicted and compared among the four methods. For climate change, the CO₂ emission was reported whereas subcritical water extraction gave the smallest amount of CO₂ emission while almost 15 times of CO₂

could be released from steam explosion due to higher energy consumption which required more electricity during the fractionation process. The second parameter, eutrophication or the nutrition enrichment of the Earth's surface, was determined by comparing nitrogen gas and phosphorus equivalents. The eutrophication took place mostly on the feedstock growth step; therefore, the efficiency of the fractionation process plays important roles on this part. Subcritical water extraction was found to show the smallest impact on eutrophication since less amount of feedstock is required for producing the same amount of the desired product. The subcritical water extraction also showed the smallest impact toward water depletion. In addition, the study indicated more than 90% of water in all four processes that was used in the feedstock growth step. The last parameter is acidification potential, where organosolve extraction and steam explosion showed smallest effects while diluted acid extraction had the highest impact on acidification potential.

4.2. Bioeconomy of bio-based product manufacturing from biomass

Besides the environmental impact, an economic aspect is very important for product development. The term bioeconomy or bio-based economy refers to an economy employing renewable bioresources such as microorganisms, agricultural crops or residues, and livestock to produce food, pharmaceuticals, energy, plastics, and other bio-based materials. In this context the utilization of lignocellulosic biomass from agricultural residues for the production of various bio-based products was explained. As shown in **Figure 8**, promising products from biomass feedstock upgrading are biogas, biofuels, biochemicals, bioplastics, carbon fiber, nanofiber,

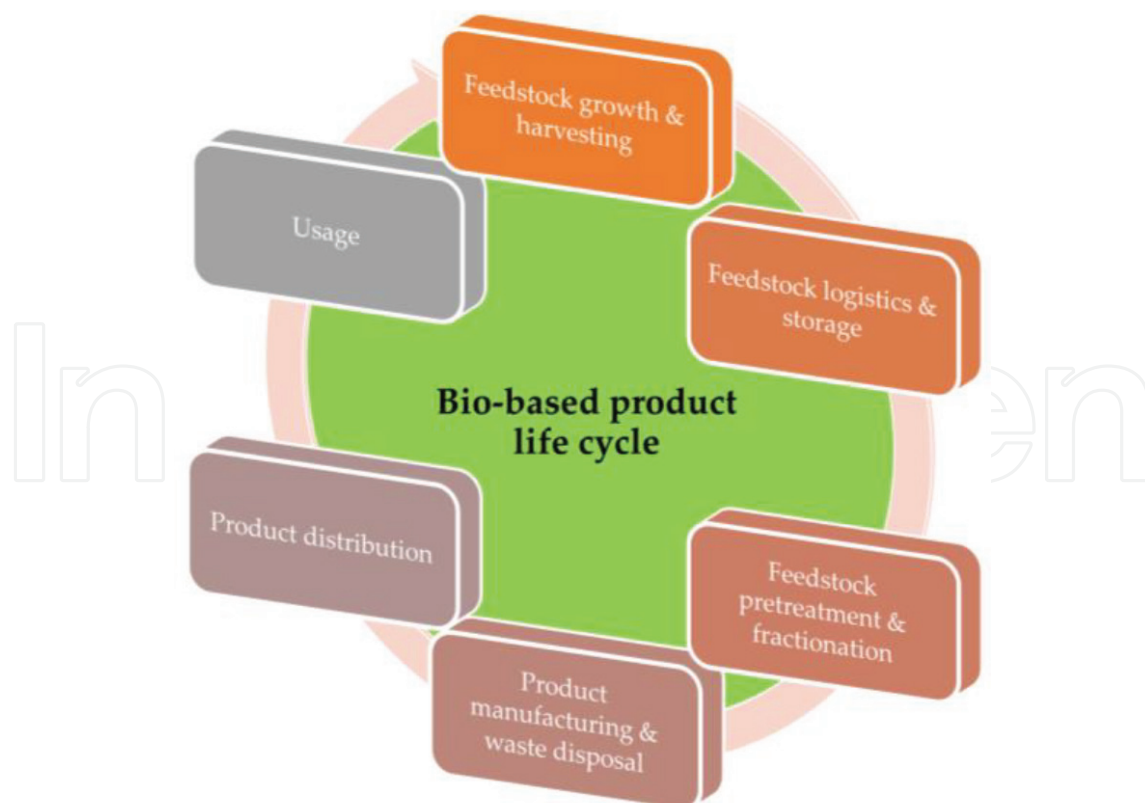


Figure 8. Life cycle of bio-based product upgraded from lignocellulosic biomass.

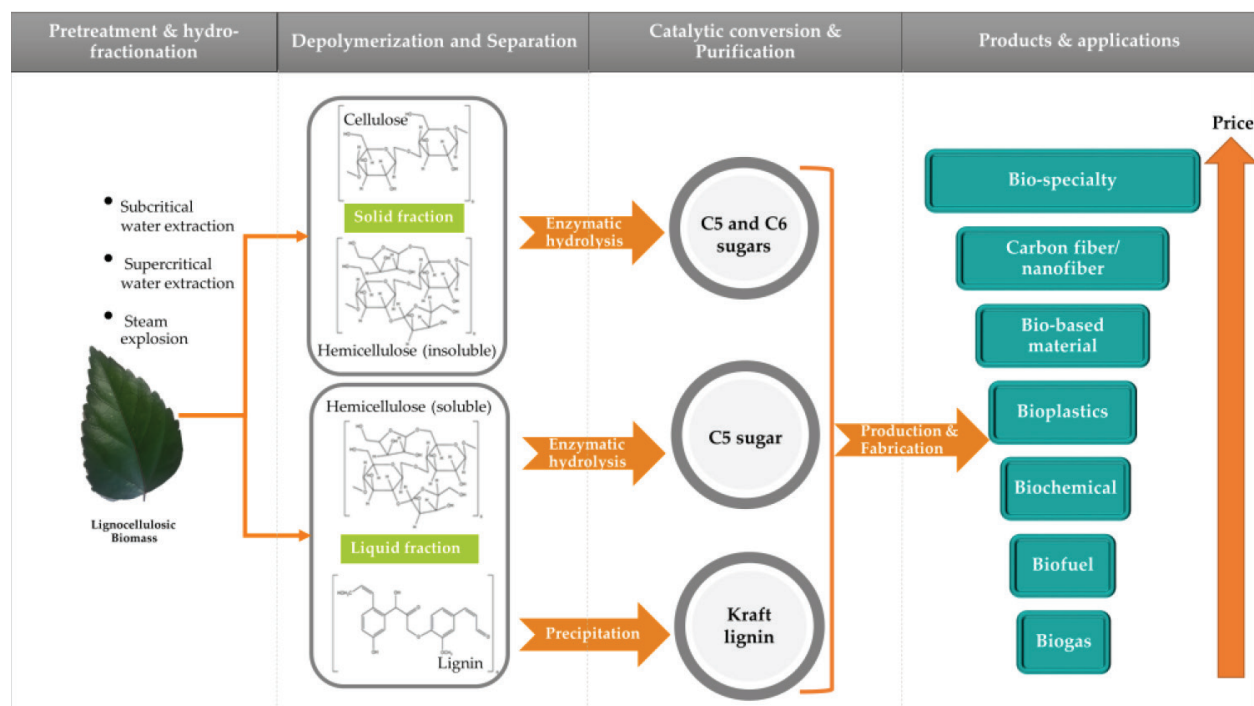


Figure 9. Bioeconomy of biomass upgrading.

and bio-specialty (a unique high-value product derived from bioresources for a specific customer group). In general, the feedstock undergoes pretreatment or hydro-fractionation to prepare the material for some particular applications. Then, the material is manufactured to produce a targeted product (**Figure 9**).

5. Conclusions

Hydro-fractionation enhanced lignin removal and provided a higher yield of sugar-based chemical platform production from biomass. The three green processes including subcritical water extraction, supercritical water extraction, and steam explosion are practical for biomass treatment. With the adjustable water properties, subcritical and supercritical water extractions are attractive tunable techniques for various bio-based compound extractions while the rapid volume expansion of water in steam explosion can destroy the high crystallinity of biopolymers. In addition, some technical feasibility in terms of energy consumption and reactor system as well as economic feasibility should be taken into consideration for future advancement.

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