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**Chapter**

# Biorefinery System of Lignocellulosic Biomass Using Steam Explosion

*Chikako Asada, Sholahuddin and Yoshitoshi Nakamura*

## Abstract

Recently, plant biomass has been attracting attention due to global warming and the depletion of fossil fuels. Lignocellulosic biomass (i.e., wood, straw, and bagasse) is attracting attention as an abundant renewable resource that does not compete with the food resources. It is composed of cellulose, hemicellulose, and lignin and is a potential resource that can be converted into high-value-added substances, such as biofuels, raw materials for chemical products, and cellulose nanofibers. However, due to its complicated structure, an appropriate pretreatment method is required for developing its biorefinery process. Steam explosion is one of the simplest and environmentally friendly pretreatments to decompose lignin structure, which converts cellulose into low-molecular-weight lignin with high efficiency. It has received significant attention in the field of not only biofuel but also biochemical production. Steam explosion involves the hydrolysis of plant biomass under high-pressure steam and the sudden release of steam pressure induces a shear force on the plant biomass. Moreover, it is a green technology that does not use any chemicals. Thus, a steam explosion-based biorefinery system is highly effective for the utilization of lignocellulosic into useful materials, such as ethanol, methane gas, antioxidant material, epoxy resin, and cellulose nanofiber.

**Keywords:** steam explosion, biorefinery, lignocellulosic, environmentally friendly, conversion

## 1. Introduction

The agricultural and forestry sectors produce the maximum amount of lignocellulosic biomass waste with minimum utilization. Moreover, many abundant crops, such as bamboo, weed, and shrubs, are not utilized optimally. Recently, lignocellulosic biomass has been widely used for burning fuel, such as gasification through the palletization process; however, the burning pathway in this process could only result in heat and a minimum amount of byproduct. Thus, the process of obtaining byproducts from lignocellulosic biomass requires considerable improvement. The utilization pathway of renewable sources for biofuels has been improved through the second generation of biofuels obtained from nonfood resources. However, the biofuel production process still results in potential waste that could have been used for obtaining another product. This opens up possibilities for the total conversion of biomass into biomaterials, pharmaceuticals, and raw chemicals with minimum waste.

Lignocellulosic biomass contains three main sources of core materials that can be developed into more valuable products: lignin, cellulose, and hemicellulose. Lignin performs biological functions such as providing mechanical support for resistance to various stresses and water transport. It is a highly irregular polymer of phenol subunits. Phenol is a derivative of the organic molecule benzene that exhibits high stability with the alcohol functional group. Lignin has recently become a promising raw material that can be converted into various products, such as biopolymer-based products (i.e., lignin-epoxy resin (LER), polyphenols sources, antioxidants, and various chemicals (i.e., 5-hydroxymethyl furfural (HMF) and furfural). Meanwhile, cellulose is a promising raw material for second-generation biofuel and has been widely used as a source of biomaterials, such as cellulose nanofiber (CNF), which can change the dominancy of conventional fillers for composites and performs other functions in biomedical and other industries. Hemicellulose has long been used as a source for monosaccharides, such as xylose, which can produce xylitol, and various biochemicals.

Lignocellulosic biomass is difficult to treat, wherein the dominance of lignin carbohydrate-complex (LCC) causes the recalcitrance of the separation process. Steam explosion is an environmentally friendly physiochemical pretreatment widely used for lignocellulosic biomass, which only uses water. This section illustrates the biorefinery process of obtaining lignocellulosic biomass from various sources and provides information on developments made in the use of steam explosion pretreatment to convert lignocellulosic biomass into value-added products, such as various biofuels, derivative methane gas, biopolymers, raw material, biochemical, and polyphenol.

## 2. Steam explosion pretreatment

In 1926, the steam explosion was introduced to efficiently process lignocellulosic biomass into fibers [1, 2], and in 1932, Babcock was patented as the first method for producing sugar and alcohol from wood chips under high pressure and temperature with varying retention time, where the chips were suddenly discharged through
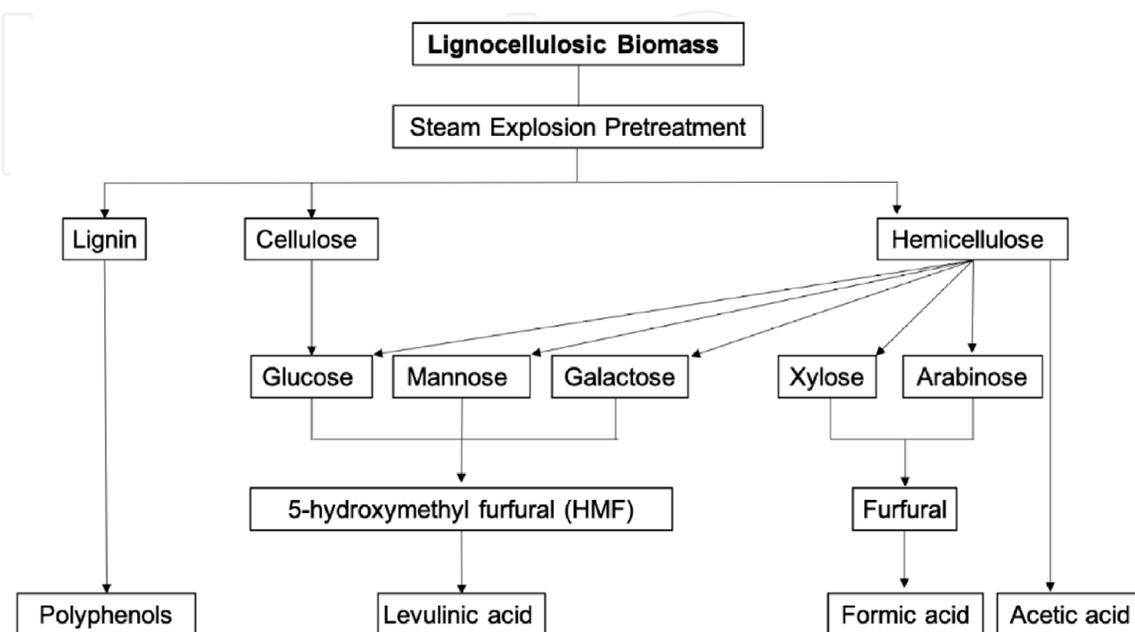


**Figure 1.**
*Route changes in the steam-exploded lignocellulosic compound.*

a slotted port and an explosion was generated [3]. Steam explosion pretreatment is still being extensively used and increasing the scope of lignocellulosic biomass utilization.

Steam explosion is classified as a psychochemical pretreatment that can change a compound and chemical structure. The autohydrolysis mechanism involved in steam explosion facilitates mechanical cutting and fiber defibrillation, which hydrolyze some of the cell-wall components and release acid in the process. The structural components are broken by the diffusion process under the induced pressure and heat that penetrate the recalcitrant of the cell wall; furthermore, the pressure released in the explosion process separates the fibers through sudden evaporation of the condensed moisture. As shown in **Figure 1**, during the steam explosion pretreatment, the biomass changes the main route as follows: lignin to low-molecular-weight lignin (LML) and polyphenols; cellulose to glucose; and hemicellulose to acetic acid, glucose, xylose, and other monosaccharides. Glucose, mannose, and galactose continue to be converted into HMF, and levulinic acid, xylose, and arabinose continue to be converted into furfural and formic acid.

## 3. Conversion concept

Various conversion concepts using steam explosion have been introduced to obtain lignocellulosic byproducts, such as raw materials and biochemicals, as described in **Figure 2**. Generally, lignin is converted into LML and polyphenols, curing agent, and LER; holocellulose is converted into CNF and biofuels, such as ethanol and biogas; and hemicellulose is converted into monosaccharides and their derived products.

### 3.1 Green conversion

To meet the current requirements of obtaining environmentally friendly byproducts, green conversion has been introduced. This has emphasized the need of a biorefinery method that can reduce the amount of waste generated by using the sustainable development goal (SDG) program, which reduces the environmental
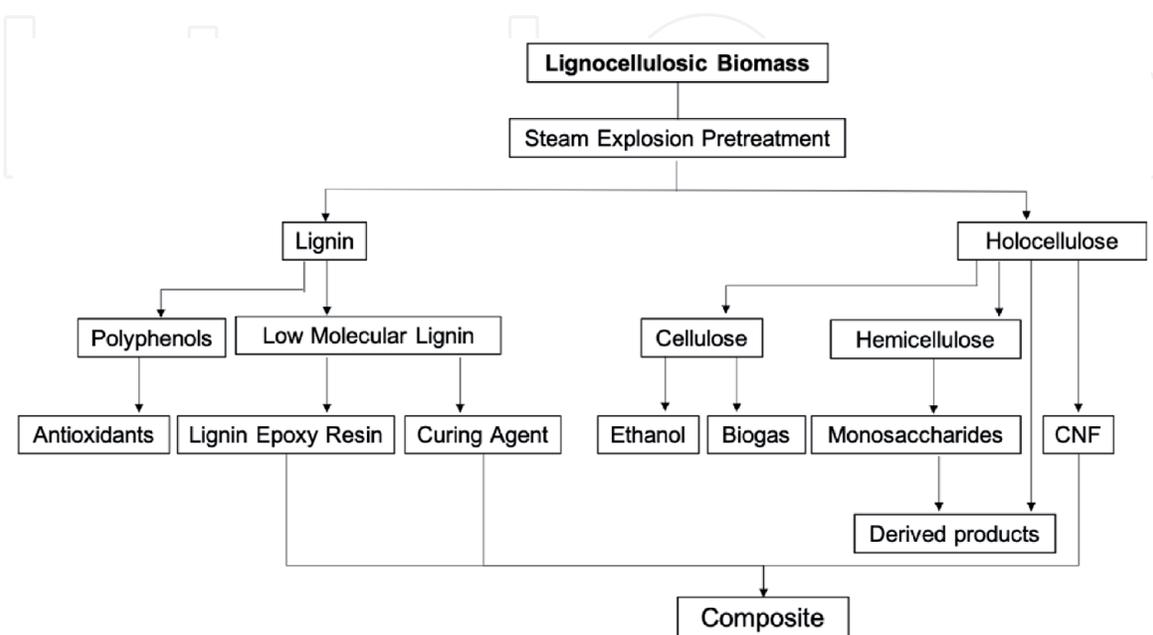


**Figure 2.**
*Conversion scheme for the main routes of steam-exploded lignocellulose.*

impact of global warming. Steam explosion pretreatment is considered environmentally friendly because it only uses pressure and water. To obtain a green conversion, various green biorefinery processes have been proposed, which produce minimum waste and reusable chemicals during the process. For example, for the conversion of lignocellulosic biomass into raw materials and biofuels, green conversion using steam explosion has been extensively reported. Ethanol production from lignocellulosic biomass follows a basic pathway: steam explosion–enzymatic saccharification–ethanol fermentation under varying steaming times and pressures with various additional methods, such as the combination of steam explosion with other pretreatments; reduction of the fermentation inhibitor, various enzymes, and their dosages; and the hydrolysis and fermentation process. Another biorefinery process for obtaining cellulose and hemicellulose byproducts, such as monosaccharides, uses the basic methods of enzymatic saccharification and combination pretreatment for ethanol production.

### 3.2 Total biorefinery

The total biorefinery concept for lignocellulosic biomass has been introduced to maximize the amount of byproduct produced from each biorefinery process and reduce waste production. A conventional biorefinery focuses on only one product from lignocellulosic biomass, such as derived products of cellulose, hemicellulose, or lignin. The waste generated from a conventional biorefinery contains a potential raw material, which is wasted into effluents; for example, the waste generated from lignocellulosic biomass ethanol production still contains lignin, which could have been used as lignin-derived products.

Asada [4] introduced a waste reduction system to obtain more useful products through steam explosion pretreatment, followed by water and methanol extraction. They used a water-soluble material for the purification process to obtain monosaccharides and oligosaccharides and methanol-soluble lignin for the resinification process to obtain LER. The two solid residues (i.e., hollocellulose and klason lignin) were used to obtain antibacterial violet pigment or lactic acid and activated carbon, respectively. The antibacterial violet pigment was produced using the enzyme saccharification process to obtain the monosaccharide content, followed by lactic acid fermentation using *Lactobacillus plantarum* and *Janthinobacterium lividum*. The waste generated from enzymatic saccharification (i.e., klason lignin) was processed into activated carbon through carbonization in a furnace at 500°C under a nitrogen gas atmosphere. Hongzang [5] examined the steam explosion-based total biorefinery process, followed by washing with water and alcohol extraction. They used a water-soluble material for the fermentation process and purified an alcohol-soluble material to obtain LML. The solid residue generated from the alcohol extraction was subjected to the pulping process, with cellulose as the final product. Asada [6] subjected Japanese cedar (*Cryptomeria japonica*) to steam explosion pretreatment followed by water extraction and methanol extraction. They used all residues obtained from each process to obtain the potential products; for example, they used the water-soluble material from water extraction for obtaining antioxidant resources by examining the antioxidant activities. Furthermore, the methanol-soluble lignin obtained from methanol extraction produced LER through epoxy resin synthesis and the hollocellulose obtained from the solid residue of methanol extraction was used for ethanol production using simultaneous saccharification and fermentation process (SSF). In another study, Asada [7] subjected cedar (*Cryptomeria japonica*), eucalyptus (*Eucalyptus globulus*), and bamboo (*Phyllostachys pubescens*) to steam explosion pretreatment, which produced raw materials by the continuous biorefinery process. They used water extraction, which produced a water-soluble material

rich in polyphenol content; the residue obtained from this process was used to continue the methanol extraction with LML as the raw material, and finally, enzymatic saccharification with glucose as the raw material was performed using the residue obtained from methanol extraction. LML was subjected to epoxy resin synthesis to produce LER. In another study, Asada [8] reported the steam explosion-based total biorefinery process for lignocellulosic biomass, followed by water extraction and acetone extraction, to produce a phenolic compound as an antioxidant, followed by acetone extraction, which produced LML. This LML was converted into LER and a curing agent. The residue obtained from the acetone extraction was used to convert hollocellulose (cellulose and hemicellulose) into CNF, with the cured epoxy resin as an end product. The final product of LER, curing agent, CNF was producing the cured epoxy resin.

## 4. Biofuels

Biofuels face competition with other food resources such as wheat, grain, corn, cassava, and palm oil. To address this issue, researchers started evaluating other renewable resources that do not face this competition. The second generation of biofuels is obtained from unutilized biomass and biomass waste resources, which are abundantly available. The biomass waste generated from agricultural and forestry sectors, such as burning fuel or dumping of disposal waste, commonly ends up with minimum utilization. Moreover, the unutilized biomass, such as weed, grass, and bamboos, can be converted into biofuels. The second-generation biofuels have been widely introduced with various biorefinery processes, including steam explosion pretreatment for bioethanol and biogas production.

### 4.1 Ethanol

The second-generation ethanol production is highly dependent on the availability of cellulose and hemicellulose from LCC. Steam explosion is an effective pretreatment for breaking LCC into cellulose and hemicellulose, which can be readily converted into ethanol. This pretreatment is widely used because of its ability to break LCC into cellulose and hemicellulose obtained from the conversion of lignocellulosic biomass into ethanol. The general routes for ethanol production via steam explosion pretreatment are described in **Figure 3**. Nakamura [9] converted rice straw into ethanol through steam explosion, followed by water extraction and enzymatic saccharification and fermentation. They reported 86% theoretical ethanol production from the substrate by using steam explosion and *Trichoderma viride* cellulase or Meicelase and *Aspergillus aculeatus cellulase* or Acucelase, using *Pichia stipites*. Sasaki [10] converted wood chips and acorns of *Quercus acutissima* into acetone, butanol, ethanol (ABE) by steam explosion pretreatment, followed by direct conversion using the separate hydrolysis and fermentation (SHF) and SSF methods. The SSF method yielded 100% ABE conversion rate, with 0.112 g/L/h ABE productivity for 196 h of incubation time with 60 g/l concentration of the initial substrate. In another study, Sasaki [11] subjected the pruned branches of pear trees to steam explosion pretreatment, followed by SSF, to produce ethanol. They compared the steam-exploded substrates with and without water and methanol extraction in terms of the amount of ethanol produced. The result showed that the SSF with water and methanol extraction achieved 76% of the theoretical production with 99.7% of glucose recovery, whereas the sample not subjected to methanol and water extraction majorly produced sugar and no ethanol. This result
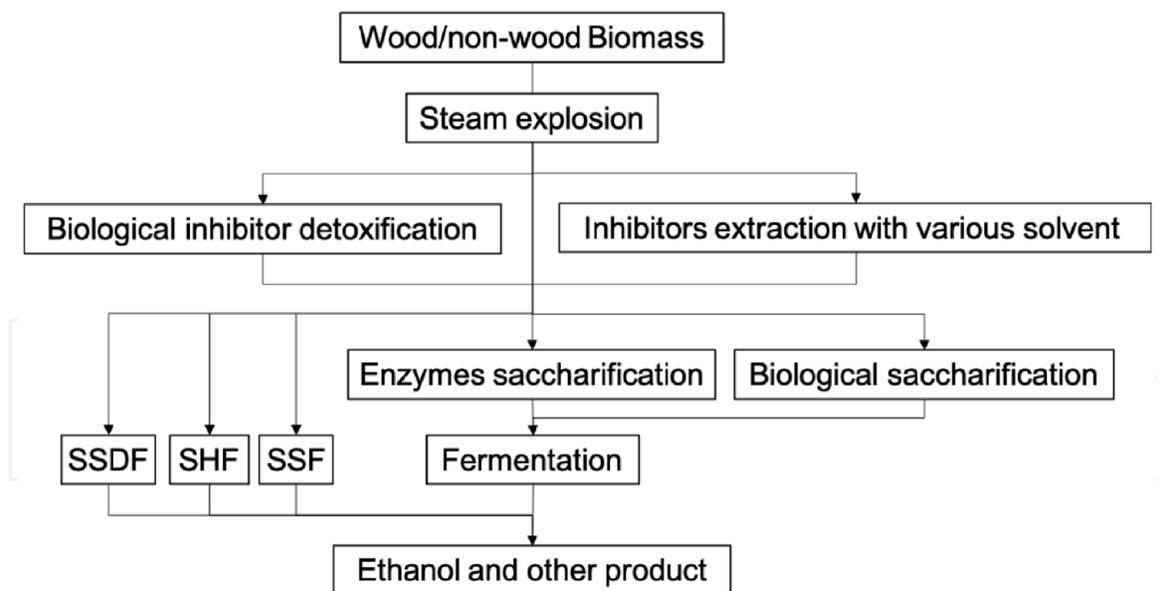
**Figure 3.**
*Production routes for ethanol produced from steam explosion.*

was attributed to fermentation inhibitors contained in the substrate as compound fractions obtained from steam explosion pretreatment.

**Table 1** shows the steam explosion-based ethanol production methods. The most significant problem incurred in ethanol production using steam explosion pretreatment is the yield of a fermentation inhibitor as a derived product of steam explosion. Ando [24] identified the influences of an aromatic monomer in steam explosion on ethanol production via *Saccharomyces cerevisiae*, which could be reduced by washing the inhibitors with a solvent, converting them into inactive compounds using biological or chemical methods, improving the steam explosion conditions to minimize the inhibitor formation, and screening for yeasts that resist the inhibitors. Asada [19] used the SSF method for spent of shitake mushroom medium for evaluating the effect of reducing the formation of fermentation inhibitors with and without water extraction. They reported 87.6% of theoretical ethanol yield, which produced 15.9 g ethanol from 100 g substrate. In another study, Asada [15] used steam explosion, followed by water extraction, in comparison with mechanical grinding with a ball mill, for converting disposable chopstick obtained from aspen into ethanol. This resulted in 20 FPU/g samples, and the continuous fermentation using the SSF method resulted in 520 and 598 mg-glucose/g-dry samples from grinding and steam explosion pretreatment, respectively. This method yielded 79% of theoretical ethanol production with 241 mg-ethanol/g-dry. In addition, Scholl [20] used steam explosion pretreatment for converting the elephant grass *Pennisetum purpureum* under various pressures and steaming times, followed by vacuum draining and washing with water to remove the inhibitor material and enzymatic saccharification using cellulase and xylanase obtained from *P. echinulatum*. Thereafter, the fermentation process was continued using *Saccharomyces cerevisiae* as the steam-exploded elephant grass, followed by water washing and using cellulose enzymes with 10 FPU/g total solid having 4 wt% substrate concentration, which did not result in a feasible production (110.45 µl/g). To overcome the toxicity of phenolic compounds obtained from the steam-exploded substrate, which act as an inhibitor for ethanol production, various treatments have been reported, such as the use of laccase produced from *Coriolopsis rigida* and *Trametes villosa*. The detoxification by laccases considerably improves the ethanol fermentation, which in turn reduces the toxic effect on *S. cerevisiae* [18]. Asada [17] converted cedar into ethanol by using steam explosion pretreatment in

| Biomass | Pretreatment | Pressures (MPa) | Steaming time (min) | Inhibitors removal | Method[*] | Enzyme and/or microorganism | | | Achievement (Glucose or ethanol yields) | References |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Saccharification | Fermentation | Other | | |
| Potato | Steam explosion | 0.51 to 3.04 | 10 | n/a | BS, SSF | *A. Awamori* | *S. cerevisiae* | | 87% | [12] |
| Rice straw | Steam explosion | 3.0 to 4.0 | 0.5 to 10 | n/a | ES, SHF | Acucelase, Meicelse | *Pichia stipitis* | | 86% | [9] |
| Domestic waste | Steam explosion | 0.5 to 2.5 | 3 | n/a | ES, SSF | *A. awamori, Trichoderma viride* NBRC 31327 | *S. cerevisiae* | | n/a | [13] |
| Japanese cedar | Steam explosion, organosolv | 2.5 to 4.5 | 5 | n/a | ES, SSF | Meicelse | n/a | | 84.4% | [14] |
| Aspen chopsticks | Steam explosion | 2.0 to 3.0 | 5 | Water extraction | ES, SSF | Meicelse | | | | [15] |
| Sawdust waste | Steam explosion | 2.5 to 5.5 | 5 | Water & Methanol Extraction | ES, SSF | Meicelase, *Trichoderma viride*, β-glucosidase | *S. cerevisiae* | | 81% | [16] |
| Japanese cedar | Steam explosion | 3.5 to 5.5 | 5 & 10 | Water extraction, Biological detoxification | ES, SSF, SSDF | Meicelase | *S. cerevisiae* BA11 | *U. thermosphaericus* A1 | 88%, 74% | [17] |
| *Q. acutissima* | Steam explosion | 3.5 | 5 | Water & Methanol Extraction | ES, SSF, SHF | Glutase-AN, Cellic CTec 2 | *C. acetobutylicum* NBRC 13948 | | 100% | [10] |
| Pear trees | Steam explosion | 2.5 to 3.5 | 5 | Water & Methanol Extraction | ES SSF | Cellic CTec 2 | *Kluveromyces marxianus* NBRC 1777 | | 76% | [11] |

| Biomass | Pretreatment | Pressures (MPa) | Steaming time (min) | Inhibitors removal | Method[*] | Enzyme and/or microorganism | | | Achievement (Glucose or ethanol yields) | References |
|---------|--------------|-----------------|---------------------|--------------------|-----------|------------------------------|--|--|------------------------------------------|------------|
| | | | | | | Saccharification | Fermentation | Other | | |
| Japanese cedar | Steam explosion | 4.5 | 3 | Water & Methanol Extraction | ES, SSF | Meicelase, *Trichoderma viride*, β-glucosidase | *S. cerevisiae* | | 70% | [6] |
| Wheat straw | Steam explosion | n/a | n/a | n/a | ES, Fermentation | Laccase | n/a | *C. rigida & T. villosa* | n/a | [18] |
| Sawtooth Oak | Steam explosion | 1.0 to 3.0 | 5 | Water extraction | SSF | Meicelase | *S. cerevisiae* AM12 | | 87.6% | [19] |
| Elephant grass | Steam explosion | 1.27 to 2.05 | 6 to 10 | Vacuum dring, Water washing | ES, Fermentation | *P. echinulatum* S1M29 | *S. cerevisiae CAT*-1 | | n/a | [20] |
| Lemon peel | Steam explosion | 0.6 | 5 | n/a | SSF, SHF | Pectinase, Cellulase, β-glucosidase (Novozym 188) | *S. cerevisiae* CECT 1329 | | n/a | [21] |
| *Brassica napus* | Steam explosion, H2SO4, CaO | n/a | n/a | n/a | ES, Fermentation | Cellulases, Xylanase | *S. cerevisiae* | | 90–93% | [22] |
| Bagasse | Steam explosion | 1.57 to 3.53 | 1 to 10 | Water extraction | ES, Fermentation | Meicelase, Acucelase | *Pichia stipitis* CBS 5773 | | n/a | [23] |

*\*BS: Biological saccharification, ES: Enzymatic saccharification, SHF: Separate hydrolysis and fermentation, SSF: Simultaneous saccharification and fermentation, SSDF: Simultaneous saccharification, detoxification, and fermentation.*

**Table 1.**
*Steam explosion-based ethanol production methods.*

comparison with water and methanol extract, followed by the use of the simultaneous saccharification, detoxification, and fermentation (SSDF) method combined with the detoxification process using *U. thermosphaericus* A1 as a biological fermentation inhibitor degrading agent to degrade the inhibitory material produced from the steam explosion pretreatment. They concluded that the fermentation inhibitor degradation in low concentration was necessary to produce ethanol from steam-exploded lignocellulosic biomass, where the steam-exploded cedar produced glucose alone due to the saccharification end product.

## 4.2 Biogas

**Figure 4** shows the cellulose conversion into methane gas. The methanogenic reaction of cellulose or other forms of carbohydrates through the hydrolysis process yields monosaccharides, which are fermented to produce acetic acid, hydrogen, and $CO_2$ [25]. From the fermented products, acetolactic methanogenesis converts the acetic acid and hydrogenotrophic methanogenesis converts the hydrogen and $CO_2$; the conversion process includes reforming the acetic acid, hydrogen, and $CO_2$ into methane [26]. Steam explosion pretreatment has been widely used for biogas production. Take [27] subjected Japanese cedar chips to 4.51 MPa steam explosion for 5 min for optimal methane production. Kobayashi [28] used bamboo to produce methane by 3.53 MPa steam explosion (243°C) using the sludge obtained from sewage treatment for microbial seed under mesophilic condition (37°C), which resulted in 80% theoretical yield with 423 ml obtained from 1 gr of cellulose and hemicellulose for 25 days of total cumulative production. Mulat [29] combined steam explosion pretreatment for lignocellulosic biomass and bioaugmentation using *Caldicellulosiruptor bescii*, which enhanced the methane production under thermophilic conditions by 140% in 50 days with low dosages of *Caldicellulosiruptor bescii* inoculum (2–5%). Sholahuddin [30] subjected rice husk to a combination of steam explosion pretreatment at 2.52 MPa and 224°C followed by water extraction and activated cow dung as the inoculum without co-digestion, at 37°C. This yielded 96.1% of stochiometric prediction of methane production with 199 ml/g of total solid, which contained 41% of cellulose only for 22 days, and all the liquid and solid residues were used as the substrate. Steam explosion pretreatment was also used for grass, such as reed, which can be used as a potential raw material for biogas because of its abundance. Lizasoain [31] subjected reed biomass (*Phragmites australis*) for biogas feedstock to steam explosion under various temperatures, pressures, and steaming times, where the 200°C and 15 min combination increased the methane yield by 85% compared to the untreated samples. Furthermore, Dererie [32] used oat straw for combined biogas and ethanol production with steam explosion pretreatment and other chemical treatment; as per the result, the residue of ethanol fermentation from steam-exploded oat straw produced higher methane than that produced by unfermented steam-exploded oat straw. They concluded that the fermentation ethanol process acts as an additional pretreatment for methane production.
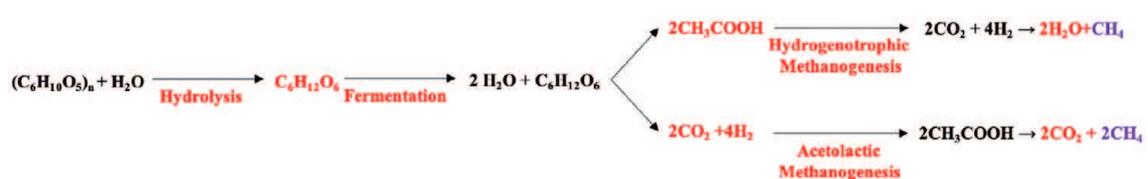


**Figure 4.**
*Cellulose conversion into methane gas.*

Methane production from lignocellulosic feedstock through steam explosion pretreatment provides a wide spectrum of total conversion. Methane is converted not only from cellulose and hemicellulose but the aromatic lignin fractions also contribute to the methane production. Moreover, steam explosion facilitates better anaerobic digestion by disrupting the lignin structure [33], which can be converted into methane. However, the anaerobic degradation of the aromatic compound incurs several difficulties in the degradation process [34], and several studies have reportedly observed anaerobic lignin degradation [35, 36]. The aromatic lignin heteropolymers mainly comprise two monolignols, which are methoxylated to various degrees: synapyl and coniferile alcohols; these monolignols are fused into lignin in the unit syringyl (S) and guaiacyl (G) forms, respectively [37]. The depolymerized monomeric unit of lignin (i.e., S) is converted into vanillin and the G unit is converted to syringaldehyde [38]. Syringaldehyde can produce a high methane yield [19, 24, 39]. Barakat [40] demonstrated the combination of xylose and the lignin fraction, such as aromatic compounds syringaldehyde and vanillin; cellulose and hemicellulose fractions, such as HMF; and furfural and xylose. The combination of xylose and syringaldehyde yielded the highest methane production, followed by the combination of xylose and furfural compared with xylose alone.

## 5. Cellulose- and hemicellulose-derived products

The cellulose- and hemicellulose-derived products by steam explosion pretreatment, such as monosaccharides, antibacterial, lactic acid, D-lactic acid, xylose, xylitol, HMF, and furfural, have been widely introduced in many studies. The production of monosaccharides as a raw material derived from cellulose- and hemicellulos-based products, such as glucose conversion, has been reported. Fernandez [41] reported the use of steam explosion for whole olive stones to enhance the enzymatic hydrolysis for conversion of cellulose into sugar. Dai [42] used steam explosion, in comparison with hydrothermal pretreatment, to convert bamboo (*Bambusa stenostachya*) into monosaccharides, such as glucose xylose and arabinose and furfural. Asada [4] reported the production of lactic acid and antibacterial through enzymatic saccharification followed by the fermentation process, and as a result, approximately 0.53 g/l where the lactic acid from glucose produced approximately 0.7 g/l from 1 g/l glucose. This result was attributed to the inhibition of the fermentation process of soluble lignin from the substrate of enzymatic hydrolysate. The antibacterial violet pigment was produced by the same process of enzymatic hydrolysate, where glucose decreased in line with the rapid cell growth, with the maximum growth occurring within 20 h. After the cell growth was stopped, the antibacterial was produced as a secondary metabolite and reached the maximum condition within 30 h, where the culture color changed into deep violet. Sasaki [43] used steam-exploded sugarcane bagasse to produce D-lactic acid by comparison with and without water extraction. They used meicelase for enzymatic saccharification and *Lactobacillus delbrueckii* NBRC 3534 for D-lactic acid fermentation; according to the result, the glucose conversion rate for water-extracted hydrolysate (49.9%) was found to be higher than that obtained without extraction (36.4%). In terms of the rate of conversion from glucose to D-lactic acid, D-lactic acid production was escalated more by the water extraction treatment (90%) than that without the extraction (66.6%). This result was attributed to the water extraction, which was decreased by fermentation inhibitors such as HMF and furfural. Macros [44] used wheat straw to produced xylose and glucose by the steam explosion pretreatment followed by warm water wash and enzymatic hydrolysis, which used a combination of accellerase and xylanase (accellerase-XC

and XY), which exhibits multiple enzyme activities, such as exoglucanase, endoglucanase, hemicellulose, and β-glucosidase. As a result, 87% and 27% increases were observed in the hemicellulose conversion into glucose and xylose, respectively. Liu [45] used simultaneous and co-fermentation for improving the xylose production by steam explosion, followed by SHF and SSCF methods. *S cerevisiae* IPE002 was used for both fermentation methods, which could convert. The glucose and xylose production reached 100.4 and 25.1 g/l concentrations, respectively. Wang [46] used corn straw to produce xylitol by acid impregnation, followed by steam explosion without detoxification; as a result, xylene hydrolysate with a high amount of xylose production and simultaneous glucan production were observed. The medium of *Candida tropicalis* produced a maximum yield of 35.6 g/l for xylitol in 38 h fermentation with 0.94 g/l h productivity.

## 6. Biomaterials

The lignocellulosic biomaterial has the potential to be used as a raw material for developing a new renewable and environmentally friendly product. The steam explosion pretreatment is a highly recommended pretreatment to obtain more valuable raw materials in the biorefinery process due to its effective breaking process, which yields lignin, cellulose, and hemicellulose byproducts. The lignocellulosic biomaterial can be used in various fields, such automobiles, medical, pharmaceutical, food packaging, beverage cans, electronics, composite industries, and the aerospace industry. The lignocellulosic biomaterials such as LER as biopolymers exhibit valuable properties, such as low moister absorption, good mechanical and electrical properties, and high chemical and thermal resistance. CNF is widely known as a raw material that exhibits good optical and mechanical properties, low thermal expansion coefficient, and high specific area. The basic properties of the raw material of lignocellulosic make it a promising raw material.

### 6.1 CNF

CNF is a promising biomaterial material that has advantageous characteristics beside those of optically transparent functional material [47], same as plastic (i.e., high gas barrier properties [48], biodegradability, light weight, high strength, ultrafine fibers, large specific surface area, low thermal expansion, characteristic viscosity in water, and environmentally friendly biomaterials, which can be used for cosmetic, biomedical, and pharmaceutical products [49–51], nanocomposites for industrial products [52], and filters that have large surface area for collecting small dust particles [53]). **Table 2** lists an extensively reported substrate developer for CNF resources; wood and nonwood biomass is the most potential CNF resource owing to the considerable abundant waste generated from the wood industry and agricultural waste.

Before isolating CNF, it is necessary to break the recalcitrant of the compact-structure LCC from wood and nonwood lignocellulose biomass before it is used as a CNF source. There are several treatments to break the LCC; in this study, steam explosion pretreatment is recognized as a promising method to obtain CNF due to its effectiveness in the biorefinery process and being considered as environmentally friendly.

After wood or non-wood lignocellulosic biomass is treated with steam explosion, two main routes have been proposed, as described in **Figure 5**. The first route is the use of the extraction process to separate the other compounds that could be used as other biomaterials, such as LML and polyphenols, by water, methanol, or acetone extraction as part of the delignification process. Then, the lignin still attached to hollocellulose is separated by the bleaching process. Several bleaching

| Biomass | Pretreatment | Condition | | Delignification | Nanosizer | References |
|---|---|---|---|---|---|---|
| | | Pressure (MPa) | Steaming time (min) | | | |
| Abaca (*Musa textilis*) | Steam explosion | 0.13 | 15 | Water, Homogenizer | Oxidation | [54] |
| Japanese cedar | Steam explosion | 3.0 to 4.0 | 5 to 15 | Water, Acetone, Bleaching (NaClO2), NaOH | Grinder | [55] |
| Yerba mate | Steam explosion | 0.15 | 60 | Water, Hydrogen peroxide, Water | Oxalic acid | [56] |
| Sugarcane bagasse | Steam explosion | 1.3 to 1.9 | 5 to 15 | Water, Immersed hydrogen peroxide, NaOH | High-speed agitation, High pressure homogenization | [57] |
| Wheat straw | Steam explosion | 3 | 2 | Water, Microwave alkali hydrolysis, NaOH | Microfluidization | [58] |
| Corncorbs | Alkaline steam explosion | n/a | n/a | NaOH, Bleaching (NaClO2) | High-speed agitation, Ultrasonication | [59] |
| Pineapple leaf | Alkaline steam explosion | 0.13 | 60 | NaOH, Acetic acid, Bleaching (NaClO2), Oxalic acid, KMnO4 | High speed mechanical stirring | [60] |
| Sugarcane bagasse | Alkaline steam explosion | 0.1 | 300 | NaOH, Hydrogen peroxide, Water, HCl | Ultrasonication | [61] |
| Sugar beet pulp | Steam explosion | 2.4 | 35 | Hydrogen peroxide, Water | High-speed agitation, Ultrasonication | [62] |
| Banana fibers | Alkaline steam explosion | 0.13 | 60 | NaOH, Acetic acid, Bleaching (NaClO2), Oxalic acid, KMnO4 | High speed mechanical stirring | [63] |
| Abaca (*Musa textilis*) | Steam explosion | 0.13 | 15 | HNO3, NaNO2, NaSO3, Water, Hydrogen peroxide | Hydrolyzed H2C2O4, Homogenization | [64] |
| Palm Oil Empty Fruit Bunches | Steam explosion | 2 | 10 | Sodium hydroxide, Water, Bleaching (NaClO2) | Grinder | [65] |
| Wheat straw | alkaline steam explosion | 0.1 | 240 | NaOH, Immersed hydrogen peroxide, HCl, Ultrasonicator, Water | Homogenizer | [66] |

| Biomass | Pretreatment | Condition | | Delignification | Nanosizer | References |
|---|---|---|---|---|---|---|
| | | Pressure (MPa) | Steaming time (min) | | | |
| Sugarcane bagasse | Steam explosion | 1.1 to 1.5 | n/a | Catalyzed hydrothermal NaOH, Bleaching, Hydrogen peroxide, Water | High-speed agitation, Ultrasonication | [67] |
| White poplar | Steam explosion | 2.5 to 3.5 | 1 to 5 | Bleaching (NaClO2), Acetic acid | Grinder | [8] |
| Rice straw | Steam explosion | n/a | n/a | NaOH, Immersed hydrogen peroxide | TEMPO-oxidized | [68] |

**Table 2.**
*CNF production via steam explosion pretreatment.*
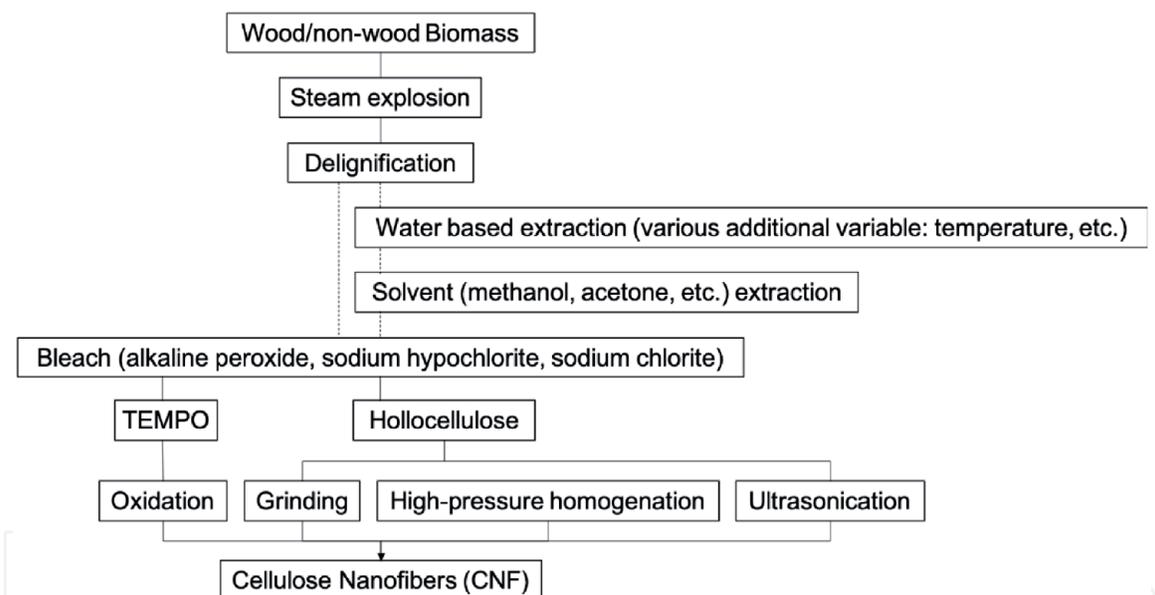


**Figure 5.**
*CNFs produced from steam explosion-based general route biorefinery.*

agents are available in the market, such as alkaline peroxide, sodium hypochlorite, and sodium chlorite, which are separated by filtration to obtain holocellulose, which is a raw material used for CNF. Hollocellulose can be directly processed to obtain CNF by using the grinding treatment [55, 69–71], high-pressure homogenization [57, 72–74], acid hydrolysis [54, 56], enzymatic hydrolysis [41, 75], and ultrasonication [67, 76, 77]. The second route is the bleaching process followed by TEMPO-mediated oxidation to isolate the CNF [68].
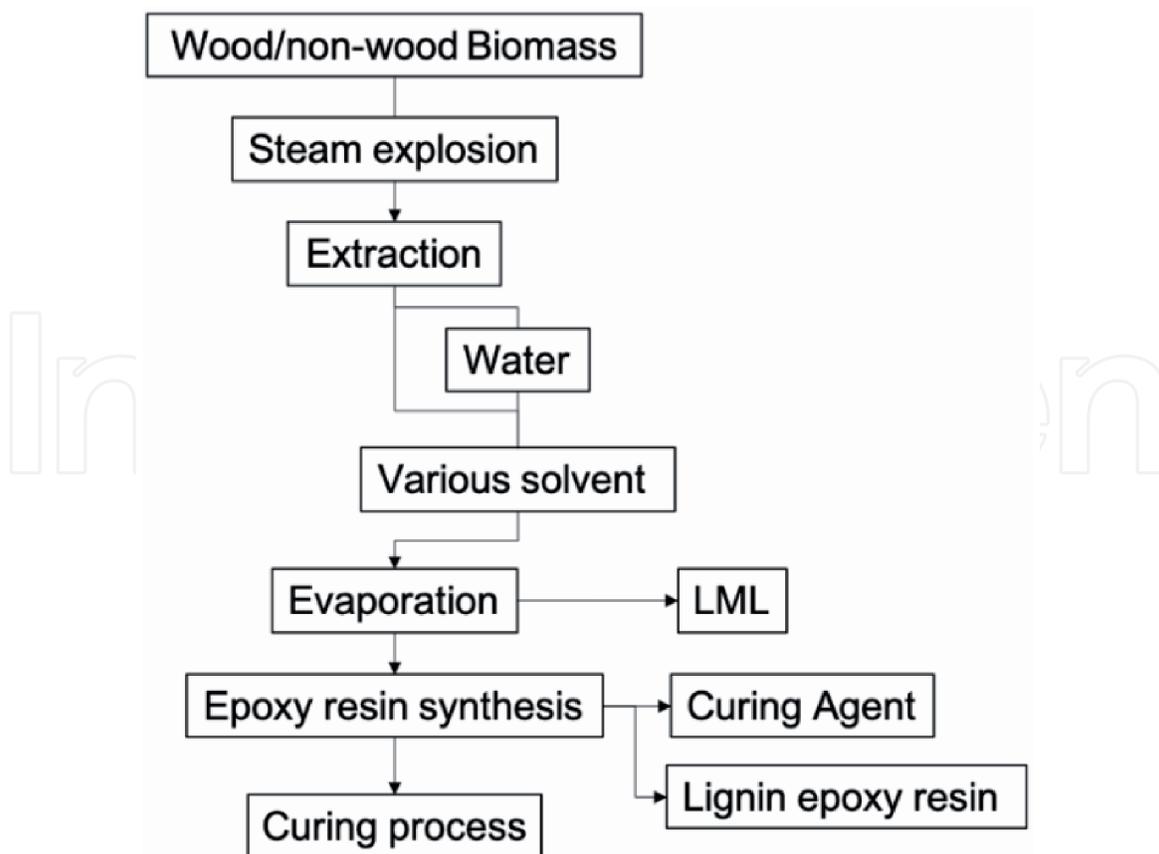
## 6.2 Biopolymers

The production of biopolymers through steam explosion pretreatment is a potential and feasible biorefinery process that can produce various polymer raw materials, such as a curing agent and lignin resin, and byproducts, such as LER

and composite material [78]. A biodegradable polymer obtained from renewable resources has recently attracted attention as a substitute for hegemony petroleum-based polymers, which support the SDG program to reduce the effect of global warming. LER production from steam-exploded lignocellulosic biomass has been extensively reported. Lignocellulosic biomass is a potential resource for epoxy resins derived from lignin and hemicellulose (i.e., lignin-based epoxies, furfural-based epoxies, and phenolic and polyphenolic epoxies). Lignin-based epoxies include depolymerized organosolv lignin [79], depolymerized hydrolysis lignin [80], LER, which acts as both a curing agent and a resin [4, 6, 7, 81–84], diglycidyl ether of vanillyl alcohol/IPDA, diglycidyl ether of methoxyhydroquinone, diglycidyl ether of vanillic acid [85], and vanillin-based epoxies [86]. Furfural-based epoxies include furan diepoxide and bis-furan di-epoxide furan monoepoxide, 2,5-Bis[(2-oxiranylmethoxy)methyl]-furan [87], 1,4-Bis[(2-oxiranylmethoxy)methyl]-benzene [88], 5,5′-Methylenedifurfurylamine (DFDA) and 5,5′-Ethylidenedifurfurylamine (CH$_3$-DFDA) [89], diglycidyl ester of 2,5-furandicarboxylic acid, 2,5-Furandicarboxyli acid, and bis(prop-2-enyl) furan-2,5-dicarboxylate [90]. The phenolic and polyphenolic epoxy resins include catechin-based (such as glycidyl ether of catechin [91], glycidyl ether of green tea extract [92], glycidyl ether of heat dried green tea extract, and glycidyl ether of freeze-dried green tea [83]) or gallic acid-based (such as gallic acid epoxidized, tannic acid epoxidized, vanillic acid epoxidized [93–95], tri- and tetra-glycidyl ethers of gallic acid [96], cardanol epoxidized [97], cardanol novolac epoxy [98], cardanol [99], and tannic acid [95]). The hard segment of lignin can provide stiffness as a lignin-cured copolymer, which can significantly affect the properties of the copolymer [78]. The curing agent allows the main adhesive to form a net or three-dimensional structure to increase the cohesive strength of the adhesive layer, which is commonly formed by acid anhydrides, amines, sulfurs, and macromolecules [100].

**Figure 6** describes the main route of lignin epoxy resin (LER) production by steam explosion-based biorefinery process. The steam-exploded substrate is subjected to the extraction process by water–methanol/acetone [4, 7, 8, 82] or direct methanol/acetone extraction under various temperatures and extraction times for water extraction. The extraction process provides LML after the evaporation process. The next step is resin synthesis using LML, which can be performed using various methods, such as a two-step reaction: epichlorohydrin catalyzed by tetrabutylammonium bromide (TBAB) to open the epoxy ring and the reaction with sodium hydroxide to reconstruct the hydrogen chloride [82]; lignin is reacted with epichlorohydrin and NaOH aqueous solution is added at 110°C, followed by the washing process, to deprive the NaOH to obtain LER [4]; lignin is reacted with epichlorohydrin and continue to use tetramethylammonium chloride (TMAC) by heated and flowed under nitrogen (N$_2$). This reaction is simpler than TBAB in order to syntheses the epoxy resin, and continue to epoxy ring reconstructed, after that the methyl ethyl ketone (MEK) solvent was used during the ring closure reaction and also for wash out the NaCl as by product of ring closure reaction [7, 8]. The curing process uses various curing agents, such as biological curing agents, epoxy resin, or chemical curing agent, to obtain cured LER through various processes. The cured process includes various biological or conventional curing agents.

LER synthesized from bamboo by steam explosion pretreatment was used for toxicity examination with human breast cancer estrogen-sensitive MCF cells. Here, the LER was synthesized from methanol-soluble lignin/LML and subjected to the epoxy reaction by melting the LML with a combination of epichlorohydrin and NAOH; then, the NaCl was produced from water extraction and evaporated to obtain epoxidized lignin. The LER production was continued by reacting with dimethyltyramine used as the curing agent. The epoxidized lignin is considered safe

**Figure 6.**
*Main routes for the conversion of lignocellulose to biopolymers by steam explosion pretreatment.*

for the toxicity effect of epoxy resin because no proliferative MCF cells are produced, which indicates the absence of endocrine-disruption activity [4]. The epoxy resin syntheses produced an LER, which can act as an epoxy resin, a curing agent, or a copolymer to produce cured epoxy resin. Sasaki [82] introduced an LER that can be used as both an epoxy resin and a curing agent, and used epoxidized lignin resin from bamboo produced through a two-step reaction with catalysis transfer method by adding bamboo lignin to TBAB-catalyzed epichlorohydrin and releasing the hydrogen chloride to reconstruct the epoxy ring in the presence of sodium hydroxide. Asada [7] produced an LER that can be used as both a curing agent and an epoxy resin, which was evaluated by the synthesis of cured epoxy resin. The LER was synthesized by dissolving LML, followed by a catalyzed process, to open the epoxy ring and detaching the hydrogen chloride used TMAC. After the separation process, continue to be dissolved with MEK as a solvent to obtain LER by the washing process and vacuum-drying.

## 7. Antioxidant resources

LCC was broken down and degraded by steam explosion. The degradation of lignin [101, 102] and its compounds [103] resulted in a complete conversion of lignin to phenolic compounds, which is also an important raw material for the production of antioxidants and drugs [101]. The depolymerization was performed through the rupture of ether and destruction of C − C bonds connecting the phenylpropane units. This method produced low-molecular-weight monomer phenols, such as 2-methoxy-phenols (guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-vinylguaiacol, 4-propyl-guaiacol, eugenol, isoeugenol, vanillin, acetovanillone, and 2-propiovanillone),

2,6-dimethoxyphenols (syringol, 4-methylsyringol, 4-allylsyringol, syringaldehyde, and acetosyringone), dihydroxybenzenes (catechol, 3-methylcatechol, 4-methyl-catechol, 3-methoxycatecho, and hydroquinone), and phenolsyringaldehyde [6, 104–110], which are comparatively easy to identify through the separation and chromatographic identification [111].

Steam explosion pretreatment for antioxidant examination for biomass has been extensively reported. Asada [8] subjected white poplar to steam explosion pre-treatment on a total biorefinery system and obtained 76 mg-catechin equiv./g-dry steam-exploded white poplar. Kurosumi [104, 112] used *S. palmata* from the leaf, stem, rhizome, and root of bamboo grass to examine its antioxidant compounds by steam explosion pretreatment followed by hot water extraction at 98°C for 2 h and methanol extraction. They examined the antioxidant activity of water-soluble material, methanol-soluble material, and its residue, which yielded a higher phenolic compound with a concentration of 217.41 mg/g from the leaf part, and expressed the antioxidant activity through butylated hydroxyanisole, which yielded 142.81 mg/g of radical scavenging activity from the leaf part. Noda [113] subjected raw garlic to steam explosion followed by water extraction to examine its antioxidant activity and obtained 0.135 g/l of $EC_{50}$ with 80.8 mg/g of phenolic compounds. Subsequently, Noda [107] examined the garlic husk in comparison steam explosion with microwave irradiation followed by water extraction, and found that the value of $EC_{50}$ was decreased, which was expressed as an increase in the radical scavenging activity. This is in line with the dramatically increased amount of phenolic compounds. Sui [114] examined the tea waste by steam explosion and observed a 20% improvement in the antioxidant capacity and OH, $O_2$, and ferric reducing antioxidant power (FRAP) radical scavenging activity of tea extracts. Romero [115] used olive leaves for obtaining the antioxidant by steam explosion pretreatment, and obtained 1950 mg of antioxidant from 100 g of olive leaves. Gong [116] used barley bran to determine the phenolic compounds and antioxidant activities with steam explosion followed by methanol extraction, and as a result, the total soluble phenolic content of 1686.4 gallic acid equivalents mg/100 g with 2983 TEAC mg/100 g of DW was obtained by the 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid method for scavenging activity and 13.45 mmol $FeSO_4 \cdot L^{-1} \cdot g^{-1}$ was obtained using FRAP. Chen [117] used steam-exploded wheat to examine the antioxidant activity and antiproliferation on HepG2 cells by ultrasonic extraction with 80% methanol, followed by washing with phosphate buffer solution. They obtained 423.335 ± 19.94 mg/ml $EC_{50}$ and concluded that the cellular and antiproliferation activities were enhanced. Furthermore, Li et al. [110] subjected the bran of buckwheat to steam explosion followed by the extraction process using 80% chilled acetone and a purification process to remove any lipid and other fractions. They examined the phenolic composition, antioxidant activity, and ability to inhibit the proliferation of HepG2 and Coca-2 cells, as well as their cytotoxicity, which resulted in 28.32 ± 0.91 and 13.18 ± 0.81 mg RE/g DW total phenolic and flavonoid, respectively. The antioxidant activity was expressed by oxygen radical absorbance capacity, which resulted in 1120.33 ± 41.43 μmol TE/g DW, and it can against the HepG2 and Caco-2 cells by antiproliferative activity. In addition, the effect of antioxidant extraction for ethanol production under the effect of saccharification and fermentation process has also been reported (e.g., [118–120]), which suggests that the scavenging activity cannot increase with the phenolic compounds. Asada [6] subjected softwood to steam explosion followed by water and methanol extraction. The water-soluble material obtained from water extraction as an antioxidant resource yielded 10.4 ± 2.52 min/μg/ml (AAPH-induced linoleic acid oxidation). This value is one-fifth that of Trolox, where the expectation was that the polyphenol compounds, such as phenylpropanoids and flavonoids, contained in water-soluble

materials exhibit an antioxidative activity equal to that of Trolox. However, the result was below expectation, which is attributed to the impurities, and thus, the softwood must be purified before being examined for antioxidant activities.

## 8. Conclusions

The steam explosion pretreatment for lignocellulosic biomass biorefinery is an environmentally friendly process and can produce a wide range of products. This system aims to obtain an effective biorefinery to identify potentialities used in all sectors, including biomedical, aviation, energy, electronics, and environment. The previously reported studies on this topic have already provided several biorefinery systems based on steam explosion pretreatment for lignocellulosic biomass. Even though the scope is beyond that of the present review, it is necessary to perform the economical calculation and life cycle assessment analysis. Further studies must be conducted as most of the abovementioned lignocellulosic biomass byproducts have not yet been produced at a commercial production level and require a transition from academic assumptions to industry assumptions.

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## Author details

Chikako Asada[1], Sholahuddin[2] and Yoshitoshi Nakamura[1*]

1 Department of Bioscience and Bioindustry, Tokushima University, Tokushima, Japan

2 Graduated School of Life and Material System Engineering, Tokushima University, Tokushima, Japan

*Address all correspondence to: ynakamu@tokushima-u.ac.jp

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