Degradation Techniques of Hemicellulose Fraction from Biomass Feedstock for Optimum Xylose Production: A Review

Budi Mandra Harahap¹

¹ Department of Agroindustrial Technology, Faculty of Agroindustrial Technology, Universitas Padjadjaran

e-mail: budi.mandra.haraph@unpad.ac.id

ABSTRACT

The utilization of xylose, one of the C-5 sugars released from hemicellulose deconstruction of biomass feedstock, is intensively studied, in particular for producing valuable fermentation products. More xylose in the initial fermentation broth is highly expected to induce more final products formed. The techniques for lignocellulose fractionation to obtain the expected xylose amount are widely developed. Nevertheless, these are slightly different from the methods for glucose production. The production of glucose is initiated by delignification to facilitate enzyme accessibility in degrading cellulose to glucose. The delignification process, however, requires harsh conditions causing further decomposition of xylose corresponded to the formation of inhibitors detected in the spent liquor of pretreatment. Hence, xylose recovery needs particular treatments and the corresponding condition. Several strategies offered attributed to xylose production involved in conventional treatment using dilute acid and other promising methods such as an autohydrolysis, solid acids, steam explosion, inorganic salt, and ionic liquid. Post-treatments by enzymatic or acid hydrolysis of xylooligosaccharides dissolved in the liquid fraction are also considered to enhance xylose recovery. This review provides such techniques and the challenges frequently arising during xylose yield optimization performed. Each method has specific benefits and drawbacks that are also addressed in this paper.

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Keywords
Biomass feedstock; degradation Techniques; hemicellulose; xylose
1. Introduction

In recent years, the depletion of fossil-fuel materials as finite and unsustainable resources becomes an attentive global problem over the world. The daily products for human’s need dominantly come from such materials. Thus, the demand of these materials increases with the rise of human population growth. This problem can be coped with finding more renewable and sustainable materials. Lignocellulose biomass is offered as the potential substitute materials because these contain valuable components [1]. The lignocellulose biomass comprises cellulose, hemicellulose, and lignin. The ratio of each component is various based on biomass types and the growth condition of the plant [2]. Sugars in cellulose and hemicellulose are potentially utilized as a fermentation substrate to produce value-added products such as bioethanol [3], xylitol [4], enzymes [5], and so on.

Cellulose is a homopolysaccharide of glucose, which is linked with 1.4-β-glycosidic bonds and has amorphous and crystalline structures [6]. On the other hand, hemicellulose contains an amorphous structure with a short polymer chain [7]. Hemicellulose is classified as a heteropolysaccharide. It consists of hexose sugars (mannose, galactose, and glucose), pentose sugars (xylose and arabinose), uronic acids, and other sugars (rhamnose and fucose) [8]. Acetyl groups also can substitute several hydroxyl groups of sugars. Therefore, when the deconstruction of hemicellulose is performed, acetic acid is also detected.

A study on the utilization of glucose as a substrate for bio-based products has been numerously reported [9]. Correspondingly, the method for glucose recovery has also been widely studied [10]. In general, glucose production steps are initiated with delignification for lignin breakage, and the process is subsequently continued by hydrolysis of pretreated solid [11]. In regards to delignification, this process required severe conditions, corresponding to high temperature, pressure, solvent concentration, and long duration [12]. Consequently, hemicellulose that has a more susceptible structure quickly wrecks [7] and then transfers to the liquid fraction in the form of monomeric and oligomeric sugars mixed with dissolved derived lignin [13].

Xylose is the most dominant C-5 sugars of hemicellulose in hardwood and grasses, which are biomass feedstock [14]. Xylose and xylooligosaccharides are secreted to liquid fraction during the delignification process [15]. Due to elevating severity level of delignification, xylose is further decomposed to furfural [16]. Consequently, the xylose amount declines. To recover xylose in a large amount, the deterrence of xylose degradation is performed by either controlling the process condition or finding more selective methods. Xylose recovery has different strategies as compared to glucose recovery. Thus, the review of the strategy to obtain more xylose is needed.

The conventional strategies to produce xylose from biomass feedstock is direct hydrolysis by dilute acid treatment assisted with heating or using the hot solution [17]. The implementation of this strategy has been considerably reported using a wide variety of biomass feedstock, such as corncob [18], corn stover [19], an oil palm frond [20], oil palm empty fruit bunches [21], and so on. Besides, the initial process, pretreatment, followed by either acid and enzymatic hydrolysis, post-treatment, is also the promising alternatives. The other treatment types considered to obtain xylose specifically are steam explosion [22], hydrothermal [23], inorganic salts [24], and ionic liquid [25]. Accordingly, this article provides a comprehensive review of the strategies to produce xylose, including undesirable product formation causing xylose reduction as well as the challenges and future development.

2. Hemicellulose Structure and Composition

Hemicellulose of biomass feedstock is predominantly present in the interior of the secondary plant cell walls [6], as depicted in Figure 1. Hemicellulose bundled with cellulose and lignin shapes the solid structure of biomass
skeleton, in particular, functioned to protect plant cells from outside interference and to mechanically and structurally support the plant tissue. The ratio of hemicellulose in specific biomass feedstock types is different depending on plant species, wood tissues, cell wall layers, growth condition climate, seasonal variation, and the crop treatment by the farmer [6]. Table 1 shows the composition of lignocellulose components in various types of biomass feedstock. In general, biomass dominantly used for biofuels, biochemical, and biomaterial production is classified into three types, viz. softwood, hardwood, and herbaceous. The sugar-based product less appropriately uses softwood as the raw materials due to high lignin content. The process will require more energy consumption to deconstruct the lignin, so its application for industrial-scale tends to be not economically feasible. On the other hand, because of higher cellulose content in hardwoods, this material is potentially used as the raw materials for the production of glucose-based products. The last type, herbaceous, contains high hemicellulose [26].

Each biomass feedstock has various polysaccharides of hemicellulose [27]. For instance, xylloglucan (XG) is found in hardwoods (Dicotyledonae and less in Monocotyledonae) and in grasses, constructed with β-D-glucosepyranosyl (β-D-Glcp) or β-D-xylanpyranosyl (β-D-Xylp) backbone as a linear chain and β-D-Galactopyranosyl (β-D-Galp), α-L-Arabinofuranosyl (α-L-Araf), α-L-Fucopyranosyl (α-L-Fucp), and acetyl as side chains [28]. Another type of hemicellulose polysaccharides is Glucuronoxylan (GX) contained in hardwoods. The GX is structured with a linear backbone of β-D-Xylp and side chains of 4-O-methyl glucuronic acid (4-O-Me-α-D-GlcpA) and acetyl [26].

Figure 1. The location of lignocellulose components in plant cell wall

The other types of hemicellulose polysaccharides are arabinoglucuronoxylan (AGX) in grasses, cereals, and softwoods, arabinoxylans (AX) in cereals, and glucuronoarabinoxylans (GAX) in grasses and cereals [26]. These polysaccharides consist of β-D-Xylp. The difference is from the side chains. The linear backbone of AGX is
substituted by 4-O-Me-α-D-GlcpA and β-L-Araf, whereas α-L-Araf and feruloy are the side chains of the AX. On the other hand, the GAX contains α-L-Araf, 4-O-Me-α-D-GlcpA, and acetyl side chain.

Due to the various substances in hemicellulose, deconstruction of this heteropolysaccharides releases various sugars such as C-5 (xylose and arabinose), C-6 (mannose, galactose, and glucose), other sugars (rhamnose and fucose), uronic acids (α-D-glucuronic, α-D-4-O-methylgalacturonic, and α-D-galacturonic acids) and acetic acids [8]. The derivative products resulted from hemicellulose degradation are given in Figure 2. When hemicellulose, particularly in monocot (grasses) and hardwood, however, are deconstructed, the monomeric sugar type of xylose is detected in liquor fraction of treatment [29]. In biomass feedstock, each xylose is linked together with a β-1.4-glycosidic bond to form a linear homogenous class of polymer, namely xylan [26]. The xylose backbone structured xylan is also substituted with acetyl, uronic acids, and other sugars.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cellulose (%dw)</th>
<th>Hemicellulose (%dw)</th>
<th>Lignin (%dw)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oil Palm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil palm mesocarp fiber</td>
<td>42.8</td>
<td>33.1</td>
<td>20.5</td>
<td>[30]</td>
</tr>
<tr>
<td>Oil palm frond</td>
<td>44.8</td>
<td>20.5</td>
<td>19.8</td>
<td>[31]</td>
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<tr>
<td>Oil palm empty fruit bunches</td>
<td>48.5</td>
<td>28.1</td>
<td>23.4</td>
<td>[32]</td>
</tr>
<tr>
<td><strong>Rice, Paddy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice husk</td>
<td>34.6</td>
<td>23.5</td>
<td>24.5</td>
<td>[33]</td>
</tr>
<tr>
<td>Rice straw</td>
<td>39.5</td>
<td>24.4</td>
<td>15.9</td>
<td>[34]</td>
</tr>
<tr>
<td><strong>Corn</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corncob</td>
<td>41.5</td>
<td>35.8</td>
<td>16.2</td>
<td>[22]</td>
</tr>
<tr>
<td>Corn stalks</td>
<td>49.2</td>
<td>25.6</td>
<td>17.2</td>
<td>[35]</td>
</tr>
<tr>
<td>Corn stover</td>
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<td>24.7</td>
<td>16.8</td>
<td>[19]</td>
</tr>
<tr>
<td><strong>Sugarcane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>37.5</td>
<td>30.6</td>
<td>25.3</td>
<td>[36]</td>
</tr>
<tr>
<td>Sugarcane straw</td>
<td>31.7</td>
<td>27.0</td>
<td>31.1</td>
<td>[37]</td>
</tr>
</tbody>
</table>

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3. Deconstruction techniques of Hemicellulose

3.1 Autohydrolysis

Autohydrolysis, also well-known as liquid hot water (LHW) is a thermal treatment using hot water set at the pressure above the saturation point [26]. This technique is highly effective to specifically obtain high xylose because of more selective degradation on hemicellulose fraction [38]. The residual solid after autohydrolysis contains a more porous and susceptible structure [39]. This structure possibly can increase the access of cellulolytic enzymes to release glucose for further use. The spent liquor as a result of this process has a low level of fermentation inhibitors as compared to dilute acid treatment [40]. Thus, the spent liquor can be directly fermented to form a valuable product. Due to the small inhibitory fraction, no detoxification step is required, so it is no need for additional operational cost. On the other hand, residual solid is hydrolysed for glucose production (Figure 3). The other advantages of autohydrolysis instead of dilute acid treatment are fewer corrosion problems, the unnecessary additional stage for neutralization, acid recycle, and precipitate removal [41].

The reason why water can extract hemicellulose is because of the process-catalyzing acid molecules formed during autohydrolysis. This process is commenced by auto-dissociation of water (H₂O), the ability of water to dissociate itself to become hydrogen (H⁺) and hydroxide (OH⁻) ions [42]. The occurrence of water auto-dissociation is stimulated by heat supply causing the increase of water conductivity. The protonation of water, furthermore, occurs by giving H⁺ ions to other water molecules, and this eventually shapes hydronium (H₃O⁺). The hydronium cleaves acetyl groups of hemicellulose to form acetic acids, which contribute to hemicellulose breakage. The presence of more acetic acids accelerates the cleavage rate of hemicellulose. Thus, the amount of xylose and dissolved sugar oligomers in the autohydrolysate rises. In addition to acetic acids, other organic acids, such as formic, uronic, levulinic acids, are also responsible for hemicellulose degradation [8].

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The research on the use of autohydrolysis treatment for xylose production of biomass feedstock has been progressively studied (Table 2). These studies have proven that autohydrolysis effectively degrades hemicellulose, releases more xylose to the autohydrolysate, and retains more cellulose in the solid fraction. The probable derivative products formed on account of hemicellulose autohydrolysis are shown in Table 2. According to this table, xylose is a dominant sugar detected in autohydrolysate, except in the feedstock of grape stalk and oil palm fronds. Moreover, the study investigated by [21] using oil palm empty fruit bunches (OPEFB) at mild autohydrolysis condition also showed a higher ratio of glucose to xylose. Hence, biomass feedstock type and operational condition affect the proportion of sugars in autohydrolysate. Finding proper biomass feedstock and optimizing operational conditions are required to obtain high xylose recovery.

The biomass feedstock is commonly autohydrolysed at the temperature range between 180 and 205 °C (Table 2). The lower temperature is given, the less xylose is obtained [43]. Higher temperature use, however, is responsible for more xylose reduction and more inhibitor formation. The way of the process optimization should avoid this. Autohydrolysis time also influences the yield of xylose and undesirable byproducts [44]. The duration corresponds to temperature use. When the autohydrolysis is conducted at high temperature, a shorter period is preferable, and vice versa. The impact of shorter and longer autohydrolysis time also occurs in the amount of xylose and unexpected byproducts. Another influential parameter is the LSR (liquid and solid ratio). Although higher LSR more likely degrades hemicellulose in a more significant amount, just a smaller amount of biomass is obtained [45]. Conversely, lower LSR could limit the mass transfer of water to the solid phase, so more hemicellulose is not optimally fractionated to the liquid phase.

In the autohydrolysate, hemicellulose is partly in the form of monomeric sugars, and the rest is still oligomer form. Hence, two-stage treatment becomes an appropriate alternative to maximize xylose recovery. Figure 3 showed the process flow diagram of two stage treatments. Principally, an oligomer formed after autohydrolysis is further decomposed to monomeric form by either acid or enzymatic hydrolysis. The research conducted by [46] reported that the liquid fraction is further hydrolyzed by 5% sulfuric acid heated to 100 °C for 90 min. Likewise, [15] used 5 N sulfuric acids at 120 °C for 45 min. On the other hand, [47] and [20] offered a more eco-friendly technique to degrade dissolved oligomer sugars by xylanase, xylan-degrading enzyme. Autohydrolysis followed enzymatic hydrolysis by xylanase effectively recovers more xylose. A challenge in xylanase use, however, is that apart from a longer and more expensive process, pure xylanase used must possess high selectivity to degrade xylan.

![Figure 3. Fractionation of cellulose and hemicellulose by autohydrolysis for xylose and glucose production](https://doi.org/10.21776/ub.jkptb.2020.008.02.01)
<table>
<thead>
<tr>
<th>Biomass Feedstock</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Severity Factor</th>
<th>Xyl (g/L)</th>
<th>Glc (g/L)</th>
<th>Ara (g/L)</th>
<th>Gal (g/L)</th>
<th>Oli-glc [g/L]</th>
<th>Oli-xyl [g/L]</th>
<th>Acetic [g/L]</th>
<th>Formic [g/L]</th>
<th>Furfural [g/L]</th>
<th>HMF [g/L]</th>
<th>Phenolic [g/L]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brewery’s spent grain</td>
<td>190</td>
<td>20</td>
<td>-</td>
<td>5.2</td>
<td>1.9</td>
<td>2.6</td>
<td>-</td>
<td>6.8</td>
<td>2.2</td>
<td>0.4</td>
<td>1.2</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>[48]</td>
</tr>
<tr>
<td>Corn cob</td>
<td>202</td>
<td>0</td>
<td>-</td>
<td>2.2*</td>
<td>0.5*</td>
<td>1.1*</td>
<td>-</td>
<td>9.2*</td>
<td>18.3*</td>
<td>0.5*</td>
<td>-</td>
<td>0.5*</td>
<td>0.1*</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>205</td>
<td>0</td>
<td>-</td>
<td>1.0*</td>
<td>0.8*</td>
<td>0.6*</td>
<td>-</td>
<td>2.2*</td>
<td>0.5*</td>
<td>0.6*</td>
<td>-</td>
<td>0.3*</td>
<td>0.0*</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Maize (Zea mays) bran</td>
<td>200</td>
<td>20</td>
<td>-</td>
<td>9.0*</td>
<td>0.8*</td>
<td>3.5*</td>
<td>2.5*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.0*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
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<td>Miscanthus x Giganteus</td>
<td>180</td>
<td>60</td>
<td>-</td>
<td>7.6*</td>
<td>0.3*</td>
<td>0.5*</td>
<td>0.2*</td>
<td>-</td>
<td>-</td>
<td>2.4*</td>
<td>-</td>
<td>1.9*</td>
<td>0.1*</td>
<td>-</td>
<td>[51]</td>
</tr>
<tr>
<td>Leucaena leucocephala</td>
<td>184</td>
<td>30</td>
<td>-</td>
<td>2.3</td>
<td>1.5</td>
<td>0.5</td>
<td>-</td>
<td>8.5</td>
<td>13.7</td>
<td>1.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>[52]</td>
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<tr>
<td>Eucalyptus globulus wood</td>
<td>-</td>
<td>-</td>
<td>3.94</td>
<td>5.6</td>
<td>0.2</td>
<td>0.4</td>
<td>-</td>
<td>1</td>
<td>10.2</td>
<td>1.2</td>
<td>-</td>
<td>0.1</td>
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<td>[53]</td>
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<tr>
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<td>2.4</td>
<td>4.3*</td>
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<td>14.6*</td>
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<td>0</td>
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<tr>
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<td>180</td>
<td>30</td>
<td>-</td>
<td>5.7</td>
<td>10.7</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
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<td>[46]</td>
</tr>
<tr>
<td>Corn Stalks</td>
<td>180</td>
<td>30</td>
<td>-</td>
<td>3.3</td>
<td>0.2</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[35]</td>
</tr>
<tr>
<td>Eucalyptus globulus wood</td>
<td>200</td>
<td>20</td>
<td>-</td>
<td>4.8*</td>
<td>0.3*</td>
<td>-</td>
<td>-</td>
<td>0.5*</td>
<td>7.0*</td>
<td>3.7*</td>
<td>-</td>
<td>2.0*</td>
<td>0.1*</td>
<td>-</td>
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<tr>
<td>Corn cob</td>
<td>200</td>
<td>30</td>
<td>-</td>
<td>1.1</td>
<td>0.1</td>
<td>0.6</td>
<td>-</td>
<td>1.8</td>
<td>25.4</td>
<td>1.3</td>
<td>-</td>
<td>0.8</td>
<td>0.2</td>
<td>-</td>
<td>[55]</td>
</tr>
<tr>
<td>Eucalyptus globulus wood</td>
<td>-</td>
<td>-</td>
<td>4.08</td>
<td>8.8</td>
<td>0.6</td>
<td>0.2</td>
<td>-</td>
<td>1.2</td>
<td>9</td>
<td>3.9</td>
<td>-</td>
<td>1.7</td>
<td>0.3</td>
<td>-</td>
<td>[56]</td>
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<tr>
<td>Sugarcane bagasse</td>
<td>170</td>
<td>45</td>
<td>-</td>
<td>2.0*</td>
<td>0.3*</td>
<td>0.3*</td>
<td>0.1*</td>
<td>0.6*</td>
<td>2.2*</td>
<td>2.0*</td>
<td>0.3*</td>
<td>1.9*</td>
<td>0.3*</td>
<td>0.2*</td>
<td>[40]</td>
</tr>
</tbody>
</table>

Note: an asterisk (*) expresses the yield of derivative products in percentage (% dw)
3.2 Dilute Acid Hydrolysis

As mentioned above, the presence of dissolved acid assisted by heat can catalyze hemicellulose degradation of solid phase to soluble monomeric and oligomeric sugars in the liquid phase. Thus, the acceleration of the hemicellulose depolymerization process can be employed by adding acids from outside. The acid-based process uses two types of acid, viz. concentrate acid and dilute acid. On the one hand, concentrate acid is effectively performed at a lower temperature, so the energy consumption for heat supply can be minimized. On the other hand, dilute acid treatment generally uses higher temperatures but the low chemical amount. Therefore, the problem associated with equipment corrosion is avoidable.

Interestingly, treatment by dilute acid, specifically degrades hemicellulose fraction at the certain process condition [18]. Accordingly, this technique includes one of the potential alternatives for xylose production. Dilute acid treatment can use both strong acids (sulfuric, hydrochloric, and nitric acids) and weak acids (oxalic, phosphoric, acetic, maleic, succinic, and citric acids). Table 3. shows acid types, and the corresponding condition to produce xylose resulted in various biomass feedstock.

The most general acid employed for producing xylose is sulfuric acid. This treatment is typically conducted at a temperature range between 116 and 170 °C for 10-90 min (Table 3). Furthermore, this acid must be diluted to the concentration interval from 0.5 to 2.5%. The use of strong concentration and more severe operational conditions possibly leads to sugar decomposition and inhibitor formation. Moreover, dilute sulfuric acid treatment is industrially more economical than stronger acids because it can reduce the use of both acids and bases for neutralization. The treatment by sulfuric acid is widely reported by various biomass materials such as corn cobs [57], [58], corn stover [19], [59], [60], oil palm empty fruit bunches [61], [62], rice straw [63], and so on.

A study conducted by [18] has proven that dilute sulfuric acid treatment can generate the highest xylose with its yield of 78.47% and retain cellulose in solid fraction to 97% as compared to lime pretreatment followed by xylanase hydrolysis and biotreatment by white-rot fungi (phanerochaete chrysosporium). Another study also proved that 0.5% of sulfuric acid could hold 78.1% glucan in the solid phase [58]. Dilute concentration of acid is an appropriate way to recover xylose because it influences sugar yield. Nevertheless, when the temperature continues increasing, the sugars formed are further degraded [17]. Higher temperature also can promote more glucose formed due to degradation of residual solid, apart from xylose reduction. Hence, this process condition must be avoided for xylose production.

Another potential acid type to recover xylose is oxalic acid. Oxalic acid includes weak acid but has a higher strength of acidity level than that in other probable weak acids such as acetic and phosphoric acid. The use of oxalic acid is less toxic than hydrochloric acid or sulfuric acid, so this technique is environmentally safer and less corrosive for equipment. As reported by [64], [65] using corncob, the optimum concentration, temperature, and time of oxalic acid treatment to reach xylose yield above 90% were 0.5-1.2%, 130-140 °C, 40-120 min, respectively.

To increase the performance of oxalic acid, another approach by the assistance of microwave affords to stimulate more xylose and its oligomer release. Microwave treatment applies an electromagnetic field to elevate the kinetic energy of inner materials by quick heat supplied from microwave radiation. Besides, microwave-assisted oxalic acid treatment gave a higher performance in hemicellulose degradation than hydrochloric and maleic acid treatments to 96 and 92% of xylose and arabinose recovery from baggage, respectively [66]. This indicated that nearly all xylan of hemicellulose was extracted and further decomposed to xylose. Moreover, the solid remains of this treatment were unaltered and able to leave more than 90% of cellulose. After cellulase degraded cellulose of

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solid residual, the conversion reached 92%. Besides that, the other acids also potentially implemented microwave-dilute acid treatment for hemicellulose deconstruction [67] such as hydrochloric acids [68], maleic acid [69], phosphoric acid on Miscanthus Sinensis [70], sulfuric acid on sugarcane bagasse [71] on rape straw [72], acetic and propionic acid on rice straw [73], or without acids, just using water on maize bran [50].

Table 3. The operational condition of dilute acid hydrolysis and the xylose yield of the liquor fraction for various biomass feedstock

<table>
<thead>
<tr>
<th>Materials (-)</th>
<th>Acid types (-)</th>
<th>Concentration (%)</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Xylose Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
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<td>20</td>
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<tr>
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<td>170</td>
<td>30</td>
<td>75</td>
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<tr>
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<tr>
<td>Giant reed</td>
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<tr>
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<td>1.2</td>
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<td>96</td>
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<tr>
<td>Corn cob</td>
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<td>40</td>
<td>94</td>
<td>[82]</td>
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<tr>
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<td>Hydrochloric acid</td>
<td>1.0</td>
<td>120</td>
<td>40</td>
<td>97</td>
<td>[84]</td>
</tr>
</tbody>
</table>

3.3 Solid Acids

Besides dilute acids, solid or super acids also is a potential alternative for hemicellulose deconstruction. The solid acids are defined as sulfuric acids with its concentration above 100% (Brønsted superacids) or acids with acidic strength higher than anhydrous aluminum trichloride (Lewis superacids) [26]. The solid acid has been discovered for a long time ago, but its utilization for hemicellulose depolymerization recently begins to be considered. It is doi https://doi.org/10.21776/ub.jkptb.2020.008.02.01
because the use of solid acids brings about several advantages such as gentle catalysts in terms of corrosiveness, safety, and waste. The proton donor is given from these acids also has high performance than that in the pure sulfuric acid. Lower temperature, water usage, energy consumption, and recyclable acids are economically feasible if this technique will be implemented on an industrial scale [85].

Various solid acids have been found with the specific purpose of use. In particular, for hemicellulose degradation, a carbon-based solid acid catalyst is highly preferable. For instance, this type of solid acid was CSO$_3$OH formed from one-step hydrothermal carbonization of microcrystalline cellulose and sulfuric acids [86]. The catalyst use of 0.25 g per 25 deionized water could give the yield of xylose to 78.1% from corncob treated at 140 °C for 6 h. The solid residue after this treatment resulted in 91.6% of cellulose hydrolysis for 48 h.

A more advanced technique of reliable acid treatment was also proposed by [87]. The solid acid used was well known as magnetic carbon-based solid acids (MMCSA) catalyst. This catalyst was synthesized by the impregnation carbonation-sulfonation process. The most striking feature of this technique was the ease of separation to reuse. Corn cob treated by this catalyst at 150 °C for 2 h was able to release 74.9% of xylose as well as 91.7% of cellulose retained in the pretreated solids. Another catalyst synthesis was also reported by [88] with additional pretreatment of the biomass feedstock. This material was soaked by a KOH aqueous solution to release the lignin. Two substances present in the dilute solution, dissolved lignin, and KOH, were evaporated at 80 °C. The concentrate solution was pyrolyzed for 2 h and then repeatedly washed by 1 M HCl and deionized water at 200°C. The result of xylose yield was 66.5%. Another type of MMCSA was C350-Cl produced from microcrystalline cellulose immersed in FeCl$_3$ [87]. This catalyst could release Fe$^{3+}$ and Cl$^-$ to degrade hemicellulose, resulting in 91.6% pentose yield from corncob. On the other hand, the Toluensulfonic acid (p-TsOH) catalyst also could remove 90% of xylan and produce a 76% sugar yield [89].

3.4 Steam Explosion

The steam explosion is a process to decompress a rigid structure of lignocellulose due to the occurrence of an explosion resulted from a sudden pressure change. Steam explosion applies three main approaches, viz. heat in the form of steam, the shear force from moisture expansion, and acid hydrolysis to degrade lignocellulose [26]. Biomass materials are heated using high-pressure steam for a few minutes until the preferable temperature below 240 °C [90]. After that, the pressure is quickly dropped to decompress the materials by explosion generated. The elements are eventually disaggregated by wrecking the inter- and intra-molecular linkage.

Numerous studies on the delignification of lignocellulose biomass favor the steam explosion as one of the best techniques [91], [92]. Such studies focused on lignin breakage to facilitate cellulase in degrading delignified biomass containing high cellulose for glucose production. Besides the objective of the steam explosion is lignin dissolution, high xylose also can be recovered by using this technique at a particular process condition.

This technique effectively induces the solubility of hemicellulose and to dissolve less lignin under controlled conditions [93]. The consequence of this steam explosion condition is that the solution is dominated by the oligomeric form of hemicellulose. It requires post-treatment to degrade hemicellulose oligomer. Besides post-treatment, pretreatment before the operation is also necessary to optimize the steam explosion performance. The pretreatment, before the steam explosion is conducted, is the impregnation of biomass with an acid catalyst such as H$_2$SO$_4$ or SO$_2$. The principle of this technique is similar to acid hydrolysis to go up expected xylose yield.

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The steam explosion was extensively used for xylose production of various biomass feedstock such as oil palm empty fruit bunches (OPEFB) [94]. This material was soaked into 0.02 M H$_2$SO$_4$ to enhance xylose release and to provide enzyme accessibility. The process was continued by steam explosion, and the result showed that the optimum yield of xylose obtained was 87.58 g/kg OPEFB under the superheated condition of the steam explosion. [22], [93], [95] also reported the use of steam explosion to recover xylose. According to [22], both high xylose yield (87.19%) and high cellulose retention in solid fraction (85.3%) are acquired after corncob was treated by the steam explosion in conjunction with acid impregnation. Xylan-derived sugars dissolved in the spent liquor were also still in the forms of oligosaccharides. For example, this treatment gave 7.15 g xylooligosaccharides per 100 g corn straw [93]. In addition, [95] reported that apart from xylose (62.8% yield), byproducts were also detected, such as HMF, furfural, and lignin-derived compounds with their yields of 0.063g, 0.075g, and less than 0.037 g per 100 g dry biomass, respectively.

3.5 Ionic Liquid

Over the past few years, ionic liquids (ILs) becomes enormous attention for most of the researchers as one of the potential techniques in fractionating lignocellulose. Ionic liquids are molten organic salts with melting points less than 100 °C and contain large cations or anions or both [96]. This liquid is increasingly being selected due to the stability of thermal treatment, high dissolving power, high selectivity, green and sustainable technology. In addition, ILs also can be applied at atmospheric pressure with the temperature reaching their decomposition points (above 200 °C) [97].

The studies on ILs are constantly scrutinized to obtain a more effective way for optimum xylose production. The typical IL type used for hemicellulose decomposition is imidazolium. For instance, an acetate containing IL (1-Ethyl-3-methylimidazolium acetate or [C$_2$ mim][OAc]) was able to produce high xylose yield (75.9%) from corn stover at low temperature (110 °C) for 3 h [98]. Its mechanism was the breakage of the hydrogen bonding network of polysaccharides. The anion of the ILs replaced inter- and intra-molecular hydrogen bonds of polysaccharides. The ILs of [C$_2$ mim][OAc] is more preferable than chloride ILs such as 1-ethyl-3-methyl-imidazolium chloride [C$_2$ mim][Cl]. Even though [C$_2$ mim][Cl] is a strong proton acceptor [99], [C$_2$ mim][OAc] brings several advantages such as lower melting temperature, a lower viscosity, and sufficient polarity.

Other types of ILs that can be considered for xylose production are 1-allyl-3-methylimidazolium formate [Amim][HCO$_3$], 1,3-dimethyl imidazolium dimethyl phosphate [Mmim][DMP], 1-ethyl-3-methylimidazolium diethyl phosphate [Emim][DEP], and 1-butyl-3-methylimidazolium hydrogen sulphate [Bmim][HSO$_4$]. The ILs of [Amim][HCO$_3$] could improve the enzymatic digestibility of the treated solid phase [25]. The xylose obtained after enzymatic hydrolysis of treated solid was 10 fold and 8 fold greater than that of untreated solid for Norway spruce and sugarcane bagasse, respectively. [100] reported that sugarcane treated by [Mmim][DMP] at 120 °C for 20 min gave xylose an enhancement of 101.12% after hydrolysis. On the other hand, the employment of [Emim][DEP] conducted at 130 °C for 12 h resulted in a high yield of reducing sugars from wheat straw [101]. This IL type also was low viscous, recyclable, and easy to synthesis, so the process was less expensive and more efficient. Finally, the ILs with type of [Bmim][HSO$_4$] yielded 16.7% (g xylose/100 g untreated xylan) at 125 °C for 82 min [102].
3.6 Inorganic salts

The last technique for xylose production introduced by this paper is inorganic salts. The inorganic salts do not contain C-H bonds and includes environmentally-friendly compounds. Principally, lignocellulose biomass is dissolved in the inorganic salt solution. The presence of salts can increase the hydrolysis rate of lignocellulose and can remove more hemicellulose [24]. As compared to dilute acid treatment, the use of salts is less corrosive and recyclable. Mild pH in the final solution can avoid the use of additional chemicals, base, for hydrolysate neutralization [103]. Thus, this could reduce the budget of chemical allocation.

Examples of inorganic salts that have evaluated are NaCl, KCl, CaCl₂, MgCl₂, FeCl₃, ZnCl₂, FeSO₄, and FeCl₃. According to [24], [104], [105], FeCl₃ was the best inorganic salt to degrade hemicellulose notably. [102] compared the performance of FeCl₃ with other mineral salts such as KCl, NaCl, CaCl₂, and MgCl₂. In this study, 0.8% FeCl₃ at 180 °C for 20 min was the most optimum salt in degrading xylotriose to xylose monomer. The implementation of this salt to biomass feedstock, such as corn stover has been conducted by [105], giving 89% xylose and xylooligosaccharide recovery, 91% hemicellulose removal, and 9% cellulose removal from solid fraction at 140 °C for 20 min with FeCl₃ concentration of 0.1%.

Another biomass feedstock treated by this salt type was miscanthus straw, resulting in 100% xylan removal at 200 °C for 15 min using 0.5% FeCl₃ [24]. According to this study, trivalent ions (Fe³⁺) had higher degradation ability than that of monovalent and divalent ions: FeCl₃ > ZnCl₂ > CaCl₂ > KCl > NaCl. The latter salt, NaCl obtained from seawater, also has been evaluated by [106] to promote hemicellulose depolymerization. The Cl⁻ was able to cleave the hydrogen bond of xylooligosaccharides. The process was assisted by microwave, giving the maximum yield of xylose to 90% at 180 °C for 10 min.

4 Conclusion

Extensive use of xylose as the second-largest sugar of several lignocellulose materials becomes an attractive study, particularly for the production of bio-based products. Xylose can be released from a solid fraction of biomass materials by particular treatments. These treatments should be able to recover more xylose, minimize further decomposition of xylose to furfural and retain more cellulose preserved in solid residue. Autohydrolysis is the simplest way to extract and deconstruct hemicellulose to xylose by hot water employment. However, this treatment required high temperature and a long time, and high oligomeric form in the spent liquor are still detected. To cope with this challenge, direct acid treatment is proposed as one of the potential alternatives.

Nevertheless, the consideration in the use of this treatment is that the process must occur under controlled conditions. The more severity factor is applied, the more xylose is further dehydrated to furfural, so the xylose amount reduces. Also, chemical cost and corrosive equipment are attentive issues to select this technique. The other methods, such as solid (super) acids, steam explosion, ionic liquid, and inorganic salts, also have both high selectivity and high degradation power. Hence, these can be considered when selecting proper and economically prospective treatment on specific biomass feedstock.

Reference


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