A review of sugarcane bagasse pretreatment for bioethanol production

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Abstract. Bioethanol is a new and renewable energy source. The second-generation bioethanol production process from lignocellulosic materials has development opportunities. This is because the first generation of bioethanol raw materials is generally a food source. Diversification of raw materials for the bioethanol production process can be developed through the use of non-food or waste sources. The process of developing bioethanol from local non-food resources or waste can increase energy security and the added value of these sources. One of the potential sources is sugarcane bagasse. The production process of bioethanol from sugarcane bagasse consists of: (i) pretreatment; (ii) enzymatic hydrolysis; (iii) fermentation; (iv) distillation; and (v) dehydration. The major composition of sugarcane bagasse consists of cellulose, hemicellulose, and lignin. Sugarcane bagasse requires a pretreatment process to separate lignin and hemicellulose from cellulose, reduce the crystallinity of cellulose and facilitate the hydrolysis of cellulose. This review focuses on sugarcane bagasse pretreatment for bioethanol production. There are several types of pretreatment processes, including (i) physical pretreatment; (ii) acid pretreatment; (iii) alkaline pretreatment; (iv) organosolv pretreatment; (v) steam explosion; and (vi) wet oxidation. Physical pretreatment is the process of physically changing the size of the sugarcane bagasse to be smaller. Chemical pretreatment is the separation process of lignin and hemicellulose from cellulose using acid compounds. Alkaline pretreatment is the separation process of lignin and hemicellulose from cellulose using alkali compounds. Organosolv pretreatment is lignocellulosic pretreatment using organic solvents. Steam explosion is the process of disrupting the complicated structure of sugarcane bagasse using steam. Wet oxidation is the process of biomass treatment with water, oxygen, or air. Steam explosion is superior to other processes in terms of hemicellulose solubilization, reaction time and no toxic substances.

1. Introduction

Bioethanol is an alternative fuel other than fossil fuels. Although the production of the first generation of bioethanol from starch materials has developed well, the production process of the second generation of bioethanol from lignocellulosic materials has development opportunities. This is because the raw material for the first generation of bioethanol is generally a food source. Diversification of raw materials for the bioethanol production process can be developed through the development of non-food sources or waste. One of the local non-food materials that have the potential to be used as raw material for renewable energy is agricultural product processing waste, namely sugarcane bagasse. Sugarcane bagasse is a solid residue from the sugarcane juice separation process. Sugarcane bagasse contains a substantial amount of carbohydrate [1].
Agricultural waste is biodegradable and lignocellulosic [2]. Sugarcane bagasse is predominantly made up of cellulose, hemicelluloses, and lignin in approximate 4:3:3 ratios [3]. Cellulose, hemicelluloses, and lignin require pretreatment processes to make the cellulose fibers more accessible to the succeeding phase of enzymatic hydrolysis, which breaks down the polysaccharides into simple sugars [4]. Pretreatment is one of the most important steps in biomass conversion since it has a direct impact on bioethanol production efficiency [5]. Pretreatment methods come in a variety of forms, including physical pretreatment, acid pretreatment, alkaline pretreatment, organosolv pretreatment, steam explosion, and wet oxidation.

2. Sugarcane bagasse composition

The composition of sugarcane bagasse is presented in table 1. Based on the table, the three main components of sugarcane bagasse are cellulose, hemicellulose, and lignin. The composition of cellulose is between 36 – 46.88%. Cellulose is the most abundant component in sugarcane bagasse. The composition of hemicellulose is between 15.91 – 28.7%. Hemicellulose is the second most abundant component in sugarcane bagasse. The composition of lignin is between 9.8 – 26.2%.

| Cellulose (%-weight) | Hemicellulose (%-weight) | Lignin (%-weight) | Others (%-weight) | References |
|----------------------|--------------------------|-------------------|------------------|------------|
| 38.9                 | 26.16                    | 23.9              | 11               | [6]        |
| 40.59                | 15.91                    | 17.5              | 26               | [7]        |
| 50                   | 27.9                     | 9.8               | 11.3             | [8]        |
| 38.2                 | 25                       | 24                | 8.3              | [9]        |
| 36                   | 28.7                     | 18                | -                | [10]       |
| 46.1                 | 20.1                     | 20.3              | 13.5             | [11]       |
| 46.88                | 22.73                    | 22.52             | -                | [12]       |
| 41.2                 | 20.2                     | 26.2              |                  | [13]       |

Sugarcane bagasse is lignocellulosic material that consists of: (i) cellulose; (ii) hemicellulose; (iii) lignin; and (iv) a small amount of pectin. Multicellular plants depend on pectin substances to hold adjacent cells together. Pectin is easily soluble in water and exists mainly in the middle and primary walls. Pectin is easily broken down by acids or enzymes, causing cells to separate. The process of cell lignification takes place in the middle lamella (ML), primary wall and secondary wall, respectively. The scheme of middle lamella, primary wall and secondary wall is presented in figure 1.

![Figure 1. The scheme of middle lamella, primary wall and secondary wall (adapted from [2]).](image-url)
In table 2, the physical properties and structures of cellulose, hemicellulose, and lignin are presented. Cellulose determines the structure of the plant cell walls. Cellulose chains are extremely structured and very cohesive with crystalline or amorphous regions [3]. The chemical treatment and heat treatment will change the shape of the crystal. The ball mill can completely destroy the crystal lattice. Cellulose accessibility refers to the difficulty of reagents in reaching the hydroxyl group of cellulose. In heterogeneous reaction, accessibility is primarily affected by the relationship between the crystalline region and the amorphous region of cellulose [14].

| Table 2. Physical properties and structure of cellulose, hemicellulose, and lignin. |
|---------------------------------|-----------------|-----------------|-----------------|
| Parameter                       | Cellulose       | Hemicellulose   | Lignin          |
| Molecular arrangement           | Well-ordered with crystalline and amorphous regions [14] | Few crystalline structure [14] | An amorphous, highly branched and heterogeneous aromatic polymer [2] |
| Degree of polymerization        | 100 – 10,000 [14] | 50–200 [3] | 4,000 [14] |
| Monomer                         | Glucose residues [14] | Saccharide molecules [14] | Coumaryl alcohol, Coniferyl alcohol, and Sinapyl alcohol [14] | Thermoplastic [14] |
| Thermal properties              | Thermal decomposition 300 – 375°C [14] | Thermal decomposition 243°C (xylan) and 332°C (arabinoxylan, xyloglucan and β-glucan) [11] | |

The chemical formula for cellulose is \((\text{C}_6\text{H}_{10}\text{O}_5)_n\), where \(n\) stands for the degree of polymerization (DP) and indicates the number of glucose units, which can range from hundreds to thousands. The solid can absorb liquid without causing any changes to the uniformity of the configuration. The solid becomes softer as the cohesion decreases and the volume increases. This phenomenon is called swellability. The swellability of cellulose is divided into swellability in the crystallization region and swellability among crystallization regions. The first is that only the swelling agent can reach the surface of the crystalline and amorphous regions. The latter refers to the fact that the crystalline region of the microfillament is impregnated with a swelling agent and then swelled to generate a new crystal lattice and display a new X-ray pattern. The unlimited swelling of cellulose is dissolution. The hydroxyl groups of cellulose are polar. As a swelling agent, the higher the polarity of the liquid, the greater the swelling degree of cellulose. Metal ions in alkaline solutions usually exist in the form of aqueous ions and are more conducive to entering the crystallization area. Usually, 15-20% NaOH will cause swelling in the crystalline region. Sodium hydroxide solutions of different concentrations and temperatures can dissolve cellulose with different degrees of polymerization [14].

Cellulose solvents can be divided into two categories, namely aqueous and non-aqueous. The aqueous solvents consist of [14]:
1. Inorganic acids such as \(\text{H}_2\text{SO}_4\) (65–80%), \(\text{HCl}\) (40–42%), \(\text{H}_3\text{PO}_4\) (73–83%), and \(\text{HNO}_3\) (84%) can cause homogeneous hydrolysis of cellulose.
2. Inorganic alkalis such as NaOH, hydrazine, and sodium zincate, and NaOH can only dissolve cellulose with low DP.

Non-aqueous cellulose solvent refers to a non-aqueous solvent-based on an organic solvent. It is composed of an activator and organic liquid. The organic solvent can be used as the active agent and as the organic solvent. It can make the solvent more polar, so that can dissolve the cellulose. Therefore, the
dissolution mechanism of cellulose in the non-aqueous solvent system cannot be easily explained by the swelling theory as in the aqueous solvent [14].

The main components of hemicellulose are Xylan, Mannan, Xyloglucan, Galactan, Arabinogalactan and Arabinan [14]. Other monosaccharide sugars in hemicelluloses include arabinose, mannose, xylose, galactose and rhamnose [2]. Hemicelluloses are grouped based on the highest residual sugar content in the polymer structure. The sugar content in hemicellulose includes: D-xylose, D-glucose, L-arabinose, D-mannose and D-galactose [3]. During pretreatment under acidic circumstances, hemicellulose is easier to extract from the cell-wall matrix than the other components [16].

Lignin is insoluble in water and acts as a binder between cellulose and hemicellulose [17]. The amorphous and crystalline structure of cellulose is clogged by lignin and hemicellulose. Removal of hemicellulose and lignin is the main factor in biomass conversion [18]. The lignin structure contains numerous polar groups and hydroxyls that can cause: (i) strong intramolecular and intermolecular hydrogen bonds; and (ii) insolubility of the inherent lignin in any solvent. The separated lignin from the condensation or degradation process can be divided into soluble lignin and insoluble lignin. The soluble lignin has an amorphous structure while the insoluble lignin has the same morphological structure as plant fibers [14].

The three main monomers of lignin are coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [14]. The monosaccharides in lignin include: pentoses (xylose, rhamnose, and arabinose), hexoses (glucose, mannose, and galactose), and uronic acids [19]. Delignification (chemical extraction of lignin) has the following effect [19]:
1. The swelling of biomass;
2. Lignin structure disruption;
3. Expansion of the internal surface area;
4. Improved accessibility of cellulolytic enzymes to cellulose fibers.

Lignin exhibits glassy transfer characteristics. Lignin is in the solid glass phase at the glassy transfer temperature. The lignin phase changes above the glassy transfer temperature. The glassy transfer temperature of separated lignin varies according to the raw materials, the separation process, the molecular weight of the lignin, and the amount of water. The temperature at which completely dried lignin softens varies from 127 to 129°C. This temperature drops dramatically as water content rises, showing that water works as a plasticizer in lignin [14].

3. Pretreatment
Biomass processing relies heavily on the removal of hemicellulose and lignin components [18]. Lignocellulosic materials have high crystallinity, so their solubility is low. Therefore, lignocellulosic materials need to undergo a decomposition process to be used as an energy source [19]. A schematic of lignocellulosic material pretreatment is presented in figure 2. Some of these decomposition processes include physical pretreatment, chemical pretreatment, etc.

![Figure 2. Schematic of lignocellulosic material pretreatment (adapted from [2]).](image-url)
3.1. Physical Pretreatment
Physical pretreatments consist of milling, immersion, washing, drying and screening. The physical pretreatments are summarized in table 3. Milling is a grinding process that obtain the desired sugarcane bagasse size and reduces cellulose crystallinity [3]. The process of soaking and washing the sugarcane are carried out through the addition of water. Drying is done so that the bagasse is dry. The drying process is carried out through the sunlight, air-dried or dryer. Screening is carried out so that the size of the bagasse is homogeneous. The size of sugarcane bagasse ranges between 0.2 and 2 mm.

| Milling          | Soaking | Washing | Drying          | Screening | References |
|------------------|---------|---------|-----------------|-----------|------------|
| √                | -       | -       | -               | < 0.5 mm  | [6]        |
| √                | -       | -       | Air-dried       | 2 mm      | [21]       |
| -                | -       | -       | Sunlight        | -         | [22]       |
| √                | 1.5 kg SCB and 31 kg water, 20 min | 3 times | 40°C – 5°C | 425 – 825 μm | [23] |
| √                | -       | -       | 105°C           | 8 – 18 mesh | [24]       |
| √                | -       | -       | Ambient temperature to approximately 10% humidity | 0.2 mm | [25] |
| √                | -       | √       | √               | 40 mesh   | [26]       |
| -                | -       | -       | Air-dried at room temperature to approximately 10% humidity | - | [27] |
| √                | √       | -       | √               | -         | [28]       |
| √                | -       | -       | 70°C – 5°C | 2 mm | [29] |
| Knife Mill       | Cold water and warm water | 60°C | 50°C | 0.5 mm | [18] |
| Knife Mill       | Hot water 50°C | 60°C | 24 hours | - | [47] |
| √                | Water until the wastewater is clear. | - | √ | - | [31] |
| √                | -       | -       | Sunlight        | -         | [32]       |
| √                | -       | 60°C    | 40 mesh         | 20 mesh   | [33]       |
| √                | -       | 24 hours | Air-dried | - | [12] |
| √                | Water   | Room temperature | 40 – 60 mesh | < 1 mm | [35] |
| √                | -       | Room temperature | 2 mm | [36] |
| √                | -       | 1 week  | -               | -         | [37]       |
3.2. Chemical Pretreatment

Chemical pretreatments consist of acid pretreatment, alkaline pretreatment, organosolv, steam explosion, and wet oxidation.

3.2.1. Acid pretreatment. Acid pretreatments are presented in Table 4. Chemicals that are generally used in the acid pretreatment process are phosphoric acid, hydrochloric acid, ferric chloride, sulphuric acid, and citric acid. Based on the table, phosphoric acid can remove hemicellulose. This is presented from the hemicellulose composition data after pretreatment. On the other hand, phosphoric acid is less effective in separating cellulose and lignin. The solubilization of hemicellulose is 97.63% [22].

HCl pretreatment can solubilize over 86% of Xylan (hemicellulose). However, HCl pretreatment has several disadvantages, namely: (i) corrosion, which necessitates the use of expensive reactor materials; (ii) the production of fermentation inhibitors; and (iii) residual particles must be neutralized before enzymatic hydrolysis and fermentation of the sugars [24].

FeCl₃ pretreatment can solubilize over 90% of Xylan (hemicellulose). FeCl₃ can produce hydronium ions which can cause depolymerization of hemicellulose to acetic and uronic acids. These acids can then catalyze the hydrolysis of hemicellulose [37].

H₂SO₄ pretreatment can solubilize over 90% of Xylan or hemicellulose. At a concentration of 10%, increasing the reaction time from 1 hour to 2 hours can increase the yield by 23%. However, it also increases operating costs by 96% [29]. At the same severity factor 3.8, an increase in temperature causes a decrease in solid yield while the hemicellulose solubilization remains constant [36]. The pretreatment process at a temperature of 100°C lasts longer than at a temperature of 205°C.

In citric acid pretreatment, increasing acid concentration and reaction time can increase the cellulose content and decrease the lignin content. Citric acid pretreatment gives a low yield on solubilization of hemicellulose. At a temperature of 100°C and a time of 90 minutes, it can solubilize 11% of hemicellulose [32].

3.2.2. Alkaline pretreatment. Alkaline pretreatments are presented in Table 5. Chemicals that are generally used in the acid pretreatment process are NaOH; Na₂CO₃; Na₂SO₃; Na₂O₂ and MgSO₄; NaOH and formaldehyde. At a temperature of 100°C, the optimum pretreatment conditions were at a concentration of 1 N NaOH and a reaction time of 30 minutes [26]. The use of 1% NaOH provides a significant delignification value [18]. The use of Na₂O₂ and MgSO₄ provides a significant delignification value as well as NaOH [18]. The use of NaOH and formaldehyde provides a delignification value from 45.03 to 47.29% [12].

Alkaline pretreatment is done under milder conditions than acid pretreatment. Alkaline pretreatment does not require the use of expensive materials and special designs to deal with corrosion and harsh reaction conditions [38]. The main reactions in the alkaline pretreatment process include the dissolution of lignin and hemicellulose and the deesterification (saponification) of intermolecular ester bonds [39]. Alkali pretreatment breaks the cell wall through (i) dissolving of hemicelluloses, lignin, and silica; (ii) hydrolysis of uronic and acetic esters; and (iii) swelling of cellulose [40].

3.2.3. Organosolv. Organosolv is lignocellulosic pretreatment using organic solvents. Organosolv pretreatments are presented in Table 6. Organosolv pretreatment effectively removes lignin from lignocellulosic materials through partial hydrolysis of lignin bonds [30]. However, most hemicellulose sugars can also be dissolved by this process [1]. Organic solvents reduce the lignin content in the cell wall by decomposing lignin macromolecules [50]. The most common solvents used in organosolv are ethanol and glycerol. The delignification properties of crude glycerol were comparable to those of pure glycerol [27]. Ethanol is alcohol with a low-boiling point and non-toxic material. Ethanol has high effectiveness on lignocellulosic biomass and is easily recovered through the distillation process [1].
### Table 4. Acid Pretreatments.

| Chemicals | Concentration | Temperature (°C) | Time | Composition (%) | References |
|-----------|---------------|------------------|------|-----------------|------------|
|           |               |                  |      | Before Pretreatment | After Pretreatment | |
| H₃PO₄     | 0.2% H₃PO₄ SCB 5% (w/v) | 186 | 24 min. | 40.1 ± 0.93 | 27.49 ± 0.67 | 18.52 ± 0.76 | 58.06 ± 1.78 | 1.24 ± 0.04 | 30.30 ± 0.45 | [22] |
| HCl       | 1.25% HCl 12.5% w/v | 130 | 10 min. | 45.2 Glucan | 23.6 Xylan | 21.3 Klason | 32.4 (solid) Glucan | 2.7 (liquid) Xylan | 3.1 (solid) Klason | 22.1 (liquid) Xylan | 17.9 Klason | [24] |
| FeCl₃     | 35 g SCB 1 mol/L FeCl₃ Solid-liquid 1:10 | 160 | 30 min. | 40.5 Glucan | 22.3 Xylan | 3.1 Arabinan 1.4 Galactan | 21.7 AIL 2.8 ASL | 52.8 Glucan | 0.2 Xylan | 43.6 AIL | [44] |
| H₂SO₄     | 10% Sample/ solution 1:30 (w/v) | 100 | 60 min. | 25.00 ± 0.11 | 19.14 ± 0.34 | 9.16 ± 0.46 | 66.11 ± 3.36 | 0.06 ± 0.00 | 0.36 ± 0.29 | [29] |
| C₆H₇O₇   | Citric acid 25 g SCB, liquid-solid 25 mL/g Citric acid 10% w/w | 100 | 90 min. | 39.84 ± 1.28 | 17.19 ± 0.97 | 22.25 ± 1.83 | 34.83 ± 1.12 | 15.16 ± 1.27 | 23.20 ± 0.12 | [32] |
| H₂SO₄     | 0.5 g H₂SO₄ per 100 g suspension Solid load 12.5% (w/w) Solid-liquid 1:7 | 205 | 5.1 min. | 45.5 ± 4.6 Glucan | 20.4 ± 4.2 Xylan 2.7 ± 0.2 Arabinan 1.1 ± 0.1 Galactan 2.5 ± 0.5 Mannan | 23.9 ± 1.4 Klason | 51.1 ± 0.1 Glucan | 0.6 ± 0.0 Xylan | 50.0 ± 3.3 Klason | [36] |

AIL : Acid-insoluble lignin  
ASL : Acid-soluble lignin  
SCB : Sugarcane bagasse
| Chemicals | Concentration | Temperature (°C) | Time | Before Pretreatment | After Pretreatment | References |
|-----------|---------------|------------------|------|--------------------|--------------------|------------|
| NaOH      | 1 N           | 100              | 30 min. | 44.43 ± 0.86 | 22.9 ± 0.67 | 17.52 ± 0.65 | 62.16 ± 0.87 | 18.62 ± 1.65 | 7.16 ± 0.32 | [26] |
| NaOH      | 2% NaOH + water | 80              | 2 h | 47.5 ± 0.83 Glucan | 27.2 ± 0.38 Xylan | 23.4 ± 0.7 Klasson | 63.5 ± 0.46 Glucan | 29.0 ± 0.81 Xylan | 5.4 ± 0.31 Klasson | 9.7 ± 0.1 Klasson | [45] |
| NaOH      | 2% NaOH + glycerol | Solid-liquid 1:10 | | 47.5 ± 0.83 Glucan | 27.2 ± 0.38 Xylan | 23.4 ± 0.7 Klasson | 57.7 ± 0.4 Glucan | 30.5 ± 0.82 Xylan | 5.4 ± 0.04 Klasson | 11.0 ± 0.0 Klasson | |
| Na₂CO₃    | 0.5 M, 240 mL | 140              | 80 min. | 46.1 ± 0.7 Glucan | 20.1 ± 0.9 Xylan | 20.3 ± 0.6 Klasson | 54.7 ± 1.5 Glucan | 24.4 ± 0.7 Xylan | 3.5 ± 0.6 Xylan | [11] |
| Na₂SO₃    | 0.5 M, 240 mL | 100              | 80 min. | 46.1 ± 0.7 Glucan | 20.1 ± 0.9 Xylan | 20.3 ± 0.6 Klasson | 39.5 ± 5.3 Glucan | 24.7 ± 0.2 Xylan | 2.8 ± 1.1 Xylan | [11] |
| Na₂O₂ and | Na₂O₂ (4%, w/v) + | 40              | 10 h | 40.47 | 35.24 | 23.69 | 68.10 | 22.86 | 10.53 | [18] |
| MgSO₄     | MgSO₄ (0.25%, w/v) | | | | | | | | | |
| NaOH      | 1%, w/v       | 100              | 1 h | 40.47 | 35.24 | 23.69 | 64.21 | 27.21 | 7.45 | [18] |
| NaOH      | 3%            | 50               | 4 h | 41.86 ± 0.38 Glucan | 28.45 ± 0.49 Xylan | 20.07 ± 0.02 Klasson | 58.11 ± 0.26 Glucan | 24.36 ± 0.16 Xylan | 4.29 ± 0.02 Klasson | |
| NaOH      | 0.7% w/v NaOH to reach 12% (w/v) solid content | 70 | 3 h | 61.54 ± 1.07 Glucan | 24.81 ± 1.24 Xylan | 12.46 ± 0.62 Klasson | 97.14 ± 0.23 Glucan yield | 80.77 ± 1.12 Xylan yield | 44.67 ± 0.21 Delignification % | [12] |
| NaOH and | NaOH to reach 12% (w/v) solid content | 80 | 2 h | | | | | | | |
| formaldehyde | Substrate 20% (w/v) | | | | | | | | | |
| Chemicals | Concentration | Temperature (°C) | Time | Composition (%) | References |
|-----------|---------------|------------------|------|-----------------|------------|
| AP : SCB (w/w) | 1 : 1.5 | | | | |
| | 1 : 3 | | | | |
| | 1 : 5 | | | | |
| NaOH | Sugarcane bagasse 15 g | 130 | 30 min. | 41.2 | 20.2 | 25.2 | 52.1 | 25.0 | 13.0 | 35 |
| NaOH 5% (w/w) | 140 | | | | | |
| Ethanol 60% | 150 | | | | | |
| Solid-liquid 1 :10 | 160 | | | | | |
| | 170 | | | | | |
| | 180 | | | | | |

**Notes:**
- AP : Alkaline pretreatments
- SCB : Sugarcane bagasse

| Chemicals | Concentration | Temperature (°C) | Time | Composition (%) | References |
|-----------|---------------|------------------|------|-----------------|------------|
| AP : SCB (w/w) | 1 : 1.5 | | | | |
| | 1 : 3 | | | | |
| | 1 : 5 | | | | |
| NaOH | Sugarcane bagasse 15 g | 130 | 30 min. | 41.2 | 20.2 | 25.2 | 52.1 | 25.0 | 13.0 | 35 |
| NaOH 5% (w/w) | 140 | | | | | |
| Ethanol 60% | 150 | | | | | |
| Solid-liquid 1 :10 | 160 | | | | | |
| | 170 | | | | | |
| | 180 | | | | | |

**Notes:**
- AP : Alkaline pretreatments
- SCB : Sugarcane bagasse
| Chemicals   | Concentration       | Temperature (°C) | Time  | Composition (%) | References |
|-------------|---------------------|------------------|-------|----------------|------------|
|             |         |                  |       | Before Pretreatment |            | After Pretreatment |            | References |
|             |         |                  |       | Cellulose | Hemicellulose | Lignin | Cellulose | Hemicellulose | Lignin |            |            |            |
| NaOH-ethanol | 30% v/v Liquid-solid 1:7 w/w | 195 | 20 min. | 44.94 Glucose | 28.24 Xylose | 18.93 | 66.2 ± 1.0 Glucose | 67.3 ± 1.5 | 6.1 ± 0.6 Xylose | 25.3 ± 0.2 | [1] |
| Glycerol    | Liquid-solid 5.3 mL/g | 175.8 | 49 min. | 46.36 ± 2.20 | 20.61 ± 0.19 | 23.93 ± 0.74 | 63.56 ± 4.64 | 9.29 ± 1.53 | 28.91 ± 0.49 | [27] |
| FeCl₃ - Ethanol | 0.025 mol/L FeCl₃ Ethanol-water 60/40 | 180.4 | 55 min. | 46.36 ± 2.20 | 20.61 ± 0.19 | 23.93 ± 0.74 | 60.26 ± 5.64 | 12.65 ± 0.42 | 29.12 ± 0.85 | [44] |
| Ethanol     | Ethanol-water 50% v/v | 182.7 | 40 min. | 46.36 ± 2.20 | 20.61 ± 0.19 | 23.93 ± 0.74 | 56.52 ± 0.37 | 13.04 ± 1.43 | 30.92 ± 0.14 | [30] |
| Ethanol     | 60% ethanol/H₂O 8% NaOH | 180 | 30 min. | 41.2 | 20.2 | 25.2 | 69.6 | 17.5 | 10.5 | [35] |

AIL : Acid-insoluble lignin
Table 7. Steam Explosion.

| Chemicals | Concentration/Pressure | Temperature (°C) | Time   | Before Pretreatment | After Pretreatment | References |
|-----------|-------------------------|------------------|--------|---------------------|--------------------|------------|
| Cellulose | Hemicellulose | Lignin | Cellulose | Hemicellulose | Lignin |
| Steam | 150 g SCB | 195 | 5 min. | 41.42 | 28.11 | 19.03 | 53.70 | 7.79 | 12.85 | [28] |
| Steam | SCB 50 wt.% 500 g | 195 (CSF 0.79) | 15 min. | 31.8 ± 05 Glucans | 12.2 ± 0.3 Xylans 0.8 ± 0.1 Arabinosyl residues in xylans | 5.2 ± 0.9 ASL 24.3 ± 0.4 AIL | 50.8 ± 0.6 Glucans | 2.9 ± 0.5 Xylans | 3.9 ± 0.3 ASL 30.7 ± 0.6 AIL | 200 (CSF 0.78) | 10.5 min. | 49.7 ± 0.7 Glucans | 2.8 ± 0.1 Xylans | 3.8 ± 0.3 ASL 31.1 ± 0.1 AIL | 205 (CSF 0.79) | 7.5 min. | 51.5 ± 0.4 Glucans | 3.5 ± 0.5 Xylans | 3.7 ± 0.0 ASL 29.4 ± 0.6 AIL |
| Steam | 15 bar | CSF 0.53 | 8 min. | 40.1 ± 0.4 Anhydrous xylose 2.3 ± 0.2 Anhydrous Arabinose | 21.5 ± 0.1 Anhydrous xylose | 21.5 ± 0.1 Anhydrous xylose | 23.6 ± 2.6 | 53.1 ± 0.1 Anhydrous xylose 0.5 ± 0.02 Anhydrous Arabinose | 6.1 ± 0.1 Anhydrous xylose | 3.4 ± 0.1 Anhydrous xylose 0.3 ± 0.01 Anhydrous Arabinose | 29.0 ± 1.2 |
| Steam | 17 bar | CSF 0.76 | 8 min. | 40.1 ± 0.4 Anhydrous xylose 2.3 ± 0.2 Anhydrous Arabinose | 21.5 ± 0.1 Anhydrous xylose | 21.5 ± 0.1 Anhydrous xylose | 23.6 ± 2.6 | 52.8 ± 0.5 Anhydrous xylose 23.6 ± 0.2 Anhydrous Arabinose | 3.4 ± 0.1 Anhydrous xylose 0.3 ± 0.01 Anhydrous Arabinose | 29.4 ± 5.1 |
| Steam | 60 g dry raw material | 195 | 10 min. | 39.70 ± 0.60 | 36.39 ± 0.38 | 7.37 ± 0.84 | 47.90 ± 0.44 | 12.85 ± 0.37 | 8.76 ± 0.56 | [34] |
| Steam | 200 | 10 min. | 39.70 ± 0.60 | 36.39 ± 0.38 | 7.37 ± 0.84 | 47.90 ± 0.44 | 12.85 ± 0.37 | 8.76 ± 0.56 |
| Steam | 205 | 10 min. | 39.70 ± 0.60 | 36.39 ± 0.38 | 7.37 ± 0.84 | 47.90 ± 0.44 | 12.85 ± 0.37 | 8.76 ± 0.56 |
Table 8. Wet Oxidation.

| Chemicals | Concentration/Pressure | Temperature (°C) | Time | Composition (%) | Before Pretreatment | After Pretreatment | References |
|-----------|------------------------|------------------|------|----------------|---------------------|-------------------|------------|
| Water Na₂CO₃ H₂SO₄ | 60 g SCB 2 g Na₂CO₃ 1.9 mL H₂SO₄ | 195 (pH 10) | 15 min. | 43.1 31.1 11.4 69.1 4.1 9.5 | | [48] |
| Water O₂ | 0.6 MPa O₂ 657 g SCB 3343 g water | 185 | 10 min. | 33.8 Glucan 22.0 Xylan 2.4 Arabinan 23.9 16.8 Glucan | 2.9 Xylan 0.3 Galactan 0.4 Arabinan 0.1 Mannan | 8.1 | [25] |

SCB : Sugarcane Bagasse
3.2.4. Steam explosion. The steam explosion has the potential to damage the crystallinity of cellulose [41]. Steam explosion pretreatments are presented in Table 7. The steam explosion uses chemical and physical techniques to disrupt the structure of lignocellulosic materials. This hydrothermal pretreatment method places the material at high pressure and high temperature for a short time, then rapidly decompresses the system and disrupts the fibril structure. The destruction of fibrils increases the accessibility of cellulose to enzymes during hydrolysis [42]. The complicated structure of sugarcane bagasse was disrupted by the steam explosion, allowing some components with small molecules to be easily removed by washing [28].

3.2.5. Wet oxidation. Wet oxidation is the process of biomass treatment with water, oxygen, or air at temperatures above 120°C [40]. Wet oxidation pretreatments are presented in Table 8. Wet oxidation can increase the solubility of hemicelluloses, especially Xylan and Arabinan. Wet oxidation also increases lignin solubility or delignification. This causes an increase in the amount of cellulose. Wet oxidation at low pH increases the solubility of hemicellulose [43]. Wet oxidation with oxygen solubilizes significant amounts of hemicellulose and lignin. Increasing the wet oxidation temperature from 185 to 200°C has no significant effect on the remaining hemicellulose and lignin [25].

Table 9. The comparison of pretreatment processes.

| Pretreatment     | Advantage                                      | Constraint                                      |
|------------------|-----------------------------------------------|-------------------------------------------------|
| Acid pretreatment| High degrees of hemicellulose solubilization.  | 1. Corrosive, toxic and hazardous material.      |
|                  |                                               | 2. The process takes a long time.                |
|                  |                                               | 3. The process takes place at a high temperature.|
| Alkali pretreatment| High efficiency in delignification process.    | 1. High concentrations of alkaline reagent lead to degradation and decomposition of polysaccharides. |
|                  |                                               | 2. The process takes a long time.                |
|                  |                                               | 3. The process takes place at a high temperature.|
| Organosolv       | 1. High selectivity towards lignin removal.   | 1. The process takes place at high pressure.      |
|                  | 2. There is no toxic material.                | 2. The process takes a long time.                |
| Steam Explosion  | 1. High degrees of hemicellulose solubilization.| The reaction conditions are high temperatures and pressures. |
|                  | 2. The process takes place in a short time.   |                                                 |
|                  | 3. There is no toxic material.                |                                                 |
| Wet Oxidation    | 1. High degrees of hemicellulose solubilization.| 1. The process takes place at high temperature.   |
|                  | 2. The process takes place in a short time.   | 2. Products of hydrolysis are oligomers that require further processing. |
|                  | 3. There is no toxic material.                |                                                 |

Wet oxidation primarily catalyzes the phase transfer of hemicellulose from the solid to the liquid phase. It does not catalyze the hydrolysis of released hemicellulose molecules. The products of the hydrolysis of hemicellulose in the Wet Oxidation process are oligomers of sugar that require further processing.
into monosaccharides [40]. The by-products of wet oxidation are succinic acid, glycolic acid, formic acid, acetic acid, phenolic compounds, and furfural, which can negatively affect further processing due to inhibition [42].

3.2.6. Comparison of pretreatment processes. The comparison of pretreatment processes is presented in table 9. Based on the table, steam explosion has advantages over the other four processes in terms of hemicellulose solubilization, reaction time, and the absence of toxic materials. The steam explosion operating temperature range is above the acid and alkali pretreatment. The Steam explosion temperature condition is near to the temperature conditions of organosolv and wet oxidation.

4. Conclusion

Pretreatment is a process to make cellulose fibers more accessible to the succeeding phase of enzymatic hydrolysis, which breaks down the polysaccharides into simple sugars for bioethanol production. There are several types of pretreatment processes, including (i) physical pretreatment; (ii) acid pretreatment; (iii) alkaline pretreatment; (iv) organosolv pretreatment; (v) steam explosion; and (vi) wet oxidation. Several processes in physical pretreatment include milling, soaking, washing, drying, and screening. Chemicals that are generally used in the acid pretreatment process are phosphoric acid, hydrochloric acid, ferric chloride, sulphuric acid, and citric acid. Chemical pretreatment has the advantage of high degrees of hemicellulose solubilization. However, chemical pretreatment uses corrosive, toxic, and hazardous materials. Alkaline pretreatment can reduce crystallinity, breakdown, and separate carbohydrate and lignin. It also has high efficiency in the delignification process. Nevertheless, high concentrations of alkaline reagent lead to the degradation and decomposition of polysaccharides. Organosolv exhibits high selectivity toward lignin removal, though there is a risk of operating at high pressure. Steam explosions represent high degrees of hemicellulose solubilization with non-toxic materials. Still, the reaction conditions are at high temperatures and pressure. With non-toxic material, Wet Oxidation signifies high degrees of hemicellulose solubilization. Even so, the by-products of wet oxidation are oligomers that require further processing. Steam explosion is superior to other processes in terms of hemicellulose solubilization, reaction time and no toxic substances.

5. Reference

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