A Review of the Thermal Pretreatment of Lignocellulosic Biomass towards Glucose Production: Autohydrolysis with DIC Technology

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There is increasing demand for the production of biofuels from lignocellulosic biomass. Lignocellulosic biomass consists mainly of three polymeric components: cellulose, hemicelluloses, and lignin. The separation of these components requires an effective pretreatment process to ensure high quality glucose production, and is highly influenced by several factors, including moisture content, cellulose crystallinity, lignin content, and available surface area. Over time, numerous pretreatment methods have been utilized to change the lignocellulosic fiber structure and to enhance the enzymatic saccharification of cellulose to polysaccharides. This article reviews thermal-based pretreatment of lignocellulosic fiber used for glucose production. Based on the reviewed studies, autohydrolysis of lignocellusic biomass, followed by the "Instant pressure drop (DIC)," method can be regarded as an effective pretreatment process of lignocellusic biomass.

Keywords: Lignocellulosic biomass; Glucose production; Format; Autohydrolysis; DIC technology

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INTRODUCTION

In addition to the increasing need for fuels and energy in industrial uses, the demand for the production of biofuels from lignocellulosic biomass and agro-industrial waste is increasing. The presence of large quantities of non-degradable biomass has led to a variety of environmental pollution. This situation has stimulated research to find a way out of the current fossil fuel situation by utilizing the biomass as an alternative source of energy through adequate physicochemical operations (Chandra *et al.* 2012; Virmond *et al.* 2013). Another contributing factor, in addition to the industrial market forces, is the strict environmental laws that have recently shifted the responsibility of ecological damage to the producer, thereby connecting biocompatibility to the costs of production. These laws have caused the operator to look for much more environmentally-friendly solutions. Historically, large amounts of lignocellulosic biomass have been lost either by intentional burning or natural rot. The existence of large supplies of lignocellulosic biomass could, however, produce fuel and energy to meet daily needs (Ioelovich 2015). For example, a small portion of lignocellulosic biomass has been utilized as a cellulose source in the pulp and paper industry.

Lignocellulosic biomass materials are the most abundant material in the world; sources range from forest to agricultural residues. Major components of lignocellulosic biomass include cellulose, hemicelluloses, lignin, starch, and extractives (Peng *et al.* 2012; Ioelovich 2015). The first four components account for most of the dry mass and exist as high molecular weight molecules, while extractives usually consist of a number of small molecular weight materials available only in small quantity. Collectively, cellulose, starch, and hemicelluloses can be referred as polysaccharides, and they can be hydrolyzed into their monosaccharide components through enzymatic or acid hydrolysis (Alvira *et al.* 2010; Peng *et al.* 2012).

Cellulose is a homopolymer of glucose with β,1-4 linkages, starch is a homopolymer of glucose with α,1-4 linkages, and hemicelluloses are heteropolymer containing both hexose and pentose (Alvira *et al.* 2010). Lignin, on the other hand, has highly irregular polymers with three-dimensional structures built from oxygenated phenyl propane units interlinked via β,0-4 and α,0-4 aryl ether linkages. Hemicelluloses and lignin behave as a shield to both starch and cellulose in plant cell walls. Extractives, which are soluble in neutral organic solvents or water, are non-structural wood components and comprise an extraordinarily large number of individual compounds of both lipophilic and hydrophilic types (Bajpai 2015; Liu *et al.* 2015). The main purpose of these cell wall polysaccharides is to behave as structural components and provide certain functions, such as transport water into the cells (Liu *et al.* 2015).

The complexity and variability of lignocellulosic biomass physicochemical structures hinder the hydrolysis of cellulose present in biomass to biofuels. The purpose of the pretreatment process for lignocellulosic biomass is to enhance the enzymes or acids accessibility and hydrolyze the cellulose by breaking down the lignin structure and disrupting the crystalline structure of cellulose (Besombes *et al*. 2010; Peng *et al.* 2012). However, several pretreatment processes have been applied to break down cellulosic physical and chemical structure, and to enhance hydrolysis yields. Among the various pretreatment processes, steam explosion (SE) is the most commonly utilized process of lignocellulosic biomass pretreatment that treats the biomass materials structure hydrothermally. In the steam explosion, the lignocellulosic biomass is taken into the reactor and operated at a temperature of 28 °C and under atmospheric pressure. Subsequently, the reactor is pressurized to 1 MPa to 3 MPa with an increasing temperature up to 200 °C to inject the steam into the biomass material for a given duration. Then, the reactor is depressurized to atmospheric pressure and controlled the temperature of around 100 to 120 °C (Pan *et al*. 2004; Sarip *et al.* 2014). The significant drawback of SE pretreatment of the lignocellulosic biomass is the possibility of generating phenolic compounds and other toxic derivatives, such as furfural and 5-hydroxymethyl-2- furfural due to the high degree of severity, which can inhibit the susequent yields of enzymatic or acid hydrolysis (Mounir *et al.* 2014).

In recent years, there is new and efficient technology that has been utilized in various biomass treatment, namely, "*Détente Instantanée Contrôlée*" (DIC), or "*Instant Controlled Pressure Drop*" technology. The distinct difference of DIC technology over the ordinary steam explosion technology is that the DIC pretreatment involves two vacuum cycles in addition to the steam explosion. Further, the pretreatment process in the DIC method can be conducted in a short period under a controlled temperature and abrupt pressure drop (Besombes *et al*. 2010; Mounir *et al.* 2014). In the DIC pretreatment process, the biomass materials are taken in a reactor under atmospheric pressure and a temperature of 28 °C. Subsequently, the temperature is reduced to about 27 °C and the vacuum cycle is implemented. Then, the reactor is pressurized to a range of 0.5 to 0.7 MPa (5 to 7 bar) with a temperature of 170 °C for a given time duration. Afterward, another vacuum cycle for abrupt cooling is performed, causing a pressure drop and a temperature decrease to a range of 35 to 42 °C. Finally, the reactor would be returned to atmospheric temperature and pressure (Sarip *et al.* 2014). However, extensive research has been conducted to determine a suitable pretremnt process on the conversion of biomass materials into glucose (Yang *et al.* 2014; Hemsworth *et al.* 2015; Miran *et al.* 2016). The present review was conducted to summarize the information on the thermal base pretreatment process of lignocellusic biomass for glucose production.

Physicochemical Compositions of Lignocellulosic Biomass

It is important to understand the potential effect of the physicochemical processes of biomass towards its utilization. Biomass needs to be pretreated and further hydrolyzed before it can be utilized for glucose production. Understanding its internal chemical structure reveals the importance of pretreatment for the conversion of chemicals in biomass, as shown in Fig. 1.

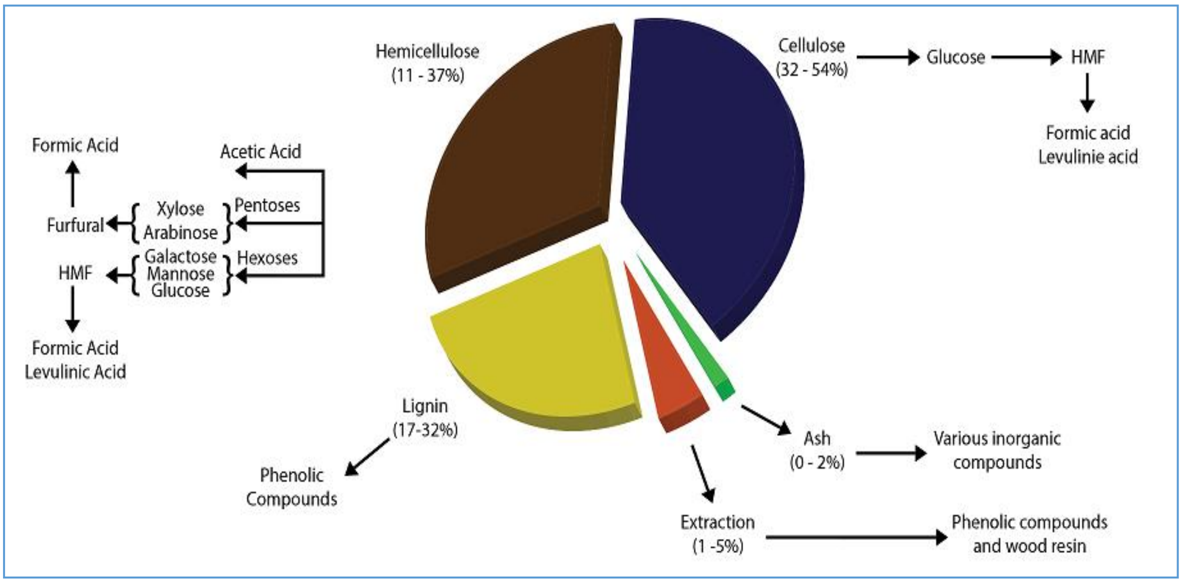


Fig. 1. Composition of lignocellulosic biomass and utilization towards value-added products

Table 1. Chemical Composition of Typical Lignocellulosic Materials (Zugenmaier 2008)

Source	Composition (%)			
	Cellulose	Hemicelluloses	Lignin	Extractives
Hardwood	43-47	25-35	16-24	2-8
Softwood	40-44	25-29	25-31	1-5
Bagasse	40	30	20	10
Coir	32-43	1-20	43-49	4
Corncobs	45	35	15	5
Corn stalk	35	25	35	5
Cotton	95	2	1	0.4
Flax (retted)	71	21	2	6
Flax (unretted)	63	12	3	2
Hemp	70	22	6	2
Hennequen	78	4-8	13	4
Istle	73	4-8	17	2
Jute	71	14	13	2
Kenaf	36	21	18	2
Ramie	76	17	1	6
Sisal	73	14	11	2
Sunn	80	10	6	3
Wheat straw	30	50	15	5

There are two types of polysaccharides: structural polysaccharides and storage polysaccharides. Both have distinct properties due to their main function even though their compositions are similar. An important structural polysaccharide is cellulose, while starch is an important storage polysaccharide. The weight percentage of the lignocellulosic components is shown in Table 1 (Zugenmaier 2008).

Cellulose

Cellulose is the major chemical component of fibrous lignocellulosic material, followed by hemicelluloses and lignin (Alriols *et al.* 2009). Figure 2 represents the various components of lignocellulosic materials and the pathway of glucose production from cellulose.

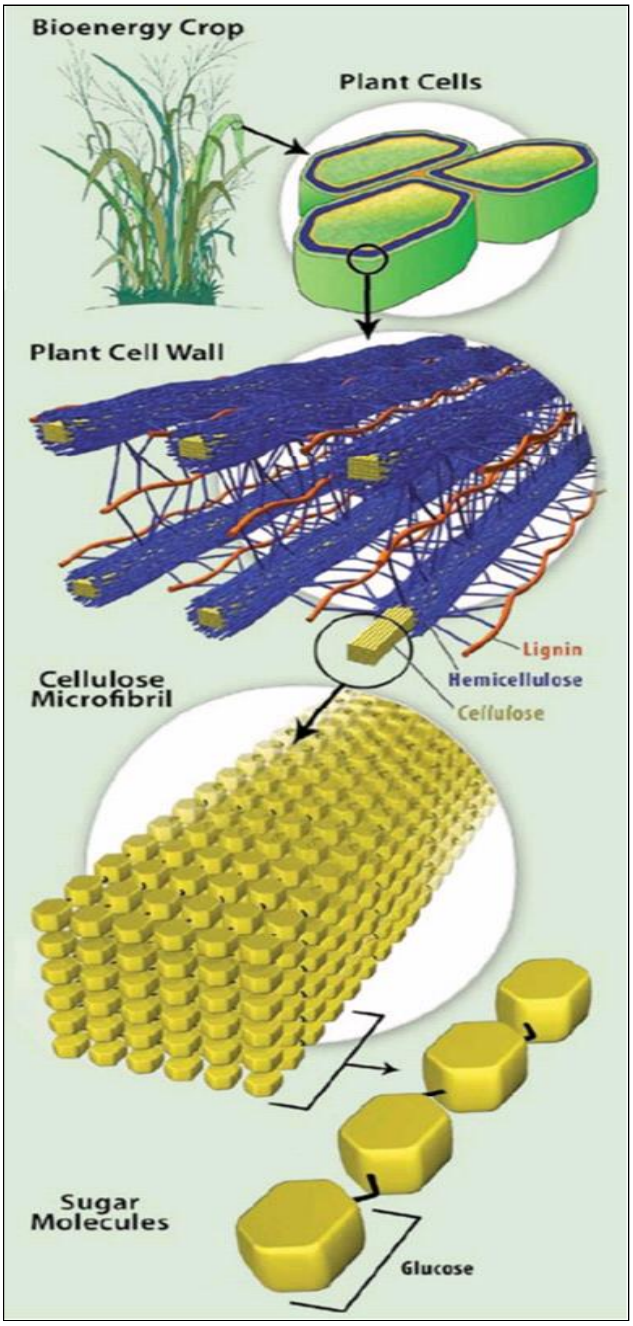


Fig. 2. An overview of plant cell structure representing the glucose production from the complex component of lignin, hemicellulose, and cellulose (Reprinted from US DOE 2014)

As can be seen in Fig. 2, cellulose microfibrils made of linear glucose polymer units are situated in the plant cell walls, forming chains known as glucan chains. These anhydroglucose units are bound together by β-(1,4)-glycosidic linkages (Deng *et al.* 2015). Due to this linkage, cellobiose is established as a repeat unit for cellulose chains, as presented in Fig. 3. Each unit of D-anhydroglucopyranose in cellulose possesses hydroxyl groups at C2, C3, and C6 positions, and is capable of undergoing reactions similar to primary and secondary alcohols (Sri Aprilia *et al.* 2016).

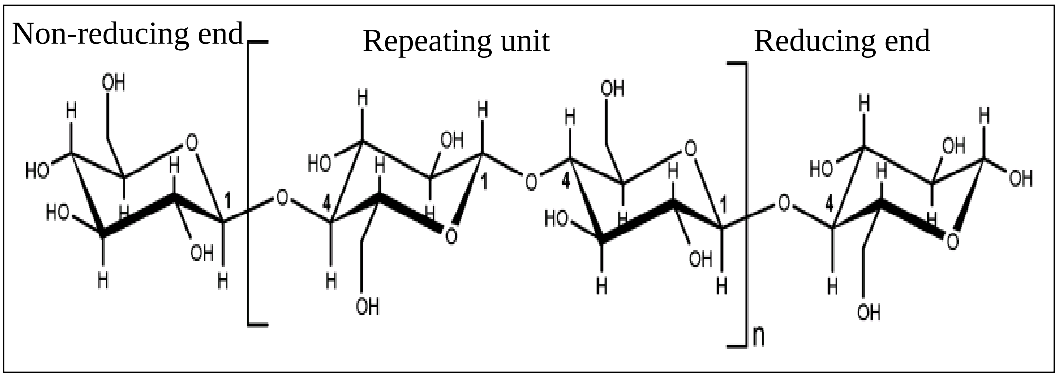


Fig. 3. Chemical structure of cellulose (Adapted from Sjostrom 1993)

Chemical and physical properties of cellulose depend on the properties of its monomer and binding properties. Cellulose exists in the form of dense crystals with extensive van der Waals attractive forces as well as hydrogen bonds, as presented in Fig. 4. However, cellulose crystals possess flexibility, unlike other crystal materials that are rigid, due to their polymeric nature in the forms of microfibrils and fibrils of cellulose. The formation of linear cellulose fibrils and microfibrils from combinations of several hundred to thousands of cellulose ribbon chains creates the structure of the plant fiber walls that have a very strong modulus due to the bonds described earlier. This makes cellulose properties different from other carbohydrates. For example, cellulose is insoluble in water and most organic solvents.

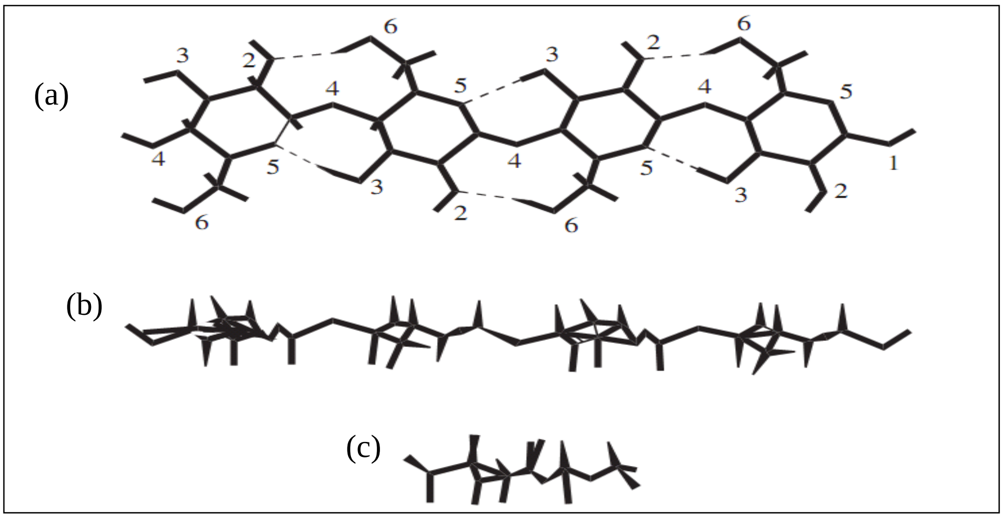


Fig. 4. Cellulose chain composed of four β-D-glucopyranose residue (cellotetraose): (a) shows the perpendicular to the flat surface of the molecule, covalent bonds, and electron clouds around the atoms; (b) shows a view of the long edge of the molecule; and (c) shows the end of the molecule (Adapted from Fengel and Wegener 1983)

Cellulose, like starch, is a monomer chain of glucose with nearly 12,000 glucose units bonded together by α-D-1,4-glycosidic bonds. Glucose in starch (helical amylase and branched amylopectin) is bonded together by α-D-1,4-glycosidic bond. The difference between α-D-1,4- and linear β-D-1,4-glucose linkage in starch and cellulose, respectively, makes it impossible for the starch digesting enzymes to digest cellulose, and leads to an enzymatic process exclusive to each. Studies have confirmed that amorphous regions between the crystallites are easily accessible to water or heavy water molecules, causing them to swell, and leading to an exchange of hydrogen between the cellulose hydroxyl groups with deuterium of the heavy water (Sun 2009; Nanda *et al.* 2015). The penetration of small molecules into the crystal lattice, however, is much more difficult and needs more time to open and widen the lattice of the cellulosic structure (Fernandes *et al.* 2011).

Hemicelluloses

Hemicelluloses consist of heterogeneous groups of polysaccharides that can exist in an amorphous form. They are fully integrated into the structure of the cellulose and located between the cellulose fibrils and lignins (Peng *et al.* 2012). The main feature differentiating hemicelluloses and cellulose is that hemicellulose have branches with short lateral chains consisting of different sugars, including pentoses (five carbon sugars: xylose, rhamnose, and arabinose), hexoses (six carbon sugars: glucose, mannose, and galactose), and uronic acids (*e.g.*, 4-*o*-methyl glucuronic, D-glucuronic, and D-galacturonic acids) (Gírio *et al.* 2010). The backbone of hemicellulose is either a homopolymer or a heteropolymer linked with by β-1,4-glycosidic bonds and occasionally β-1,3-glycosidic bonds (Bajpai 2016). The sugars are highly substituted with acetic acid. The branched nature of hemicellulose renders them amorphous and relatively easy to hydrolyze into their constituent sugars compared to cellulose. When hydrolyzed, the hemicelluloses from hardwoods release products high in xylose (a five-carbon sugar). The hemicelluloses contained in softwoods, by contrast, yield more six-carbon sugars.

Hemicelluloses are not chemically homogeneous and exist in different composition percentages, as shown in Table 2 (Lee *et al.* 1997; Xiao *et al.* 2001). Hardwood hemicelluloses contain mostly xylose or xylans, while softwood hemicelluloses contain mostly glucomannans (Matsagar *et al.* 2015). Xylans are the most abundant hemicellulose, having a backbone of β-D-xylopyranose units. The degree of polymerization of hardwood xylans is higher than in softwoods (150 to 200).

Lignin

Lignin, the other major biomass constituent, acts as a barrier to water penetration and as “glue” that holds together the cell wall. Lignin contains 3-dimensional amorphous polymers and a basic structural phenylpropane unit, as presented in Fig. 5 (Li *et al.* 2015a).

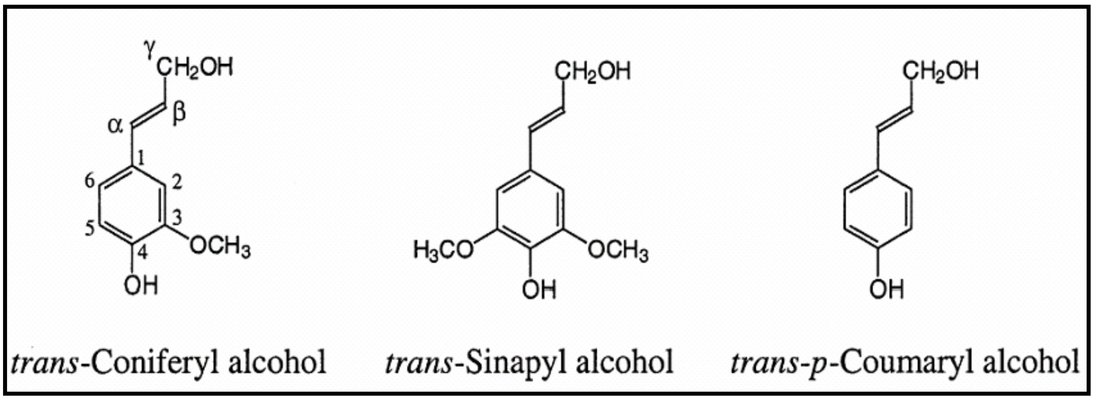
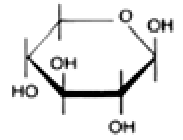
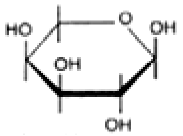
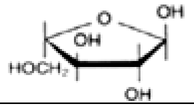
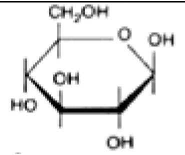
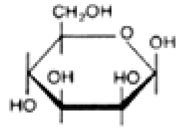
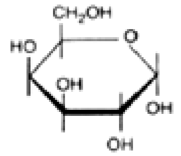
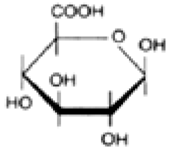
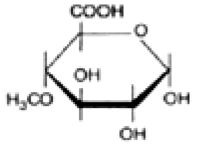
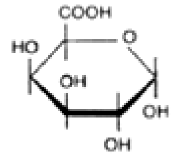
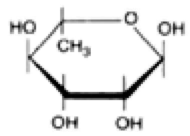
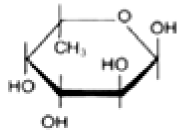


Fig. 5. Basic unit of phenylpropane composing lignin (Adapted from Kameshwar and Qin 2016).

Table 2. List of Sugar Components in Hemicelluloses (Walker *et al*. 2013)

Sugar	Chemical name	*IUPAC name*	Chemical structure
Pentose	xylose	*β-D-xylopyranose*	
	arabinose	*α-L-arabinopyranose*	
	arabinose	*α-L-arabinofuranose*	
Hexose	glucose	*β-D-glucopyranose*	
	mannose	*β-D-mannopyranose*	
	galactose	*β-D-glactopyranose*	
Uronic acid	Glucuronic acid	*β-D-glucopyranosyluronic acid*	
		α-D-4-o-methyglucuronic acid	
	Galacturonic acid	*α-D-glactopyranosyluronic acid*	
Deoxy- Hexose	*Rhamnose*	*α-L-rhamnopyranose*	
	Fucose	*α-L-fucopyranose*	

Lignin behaves as an amorphous thermoplastic polymer; if heated beyond its glass transition temperature, it becomes rubbery and enables some structural movements (Laurichesse and Avérous 2014). Once extracted from wood, lignin loses its thermoplasticity, due to severe degradation subjected to its high molecular weight and three-dimensional structure. Thermal-treated lignin will normally appear on the surface of the cellular structure of biomass (Li *et al.* 2015b).

Lignin also acts as a bulking agent, and with its rigidity and stiffness, it imparts strength to the cell wall and its surroundings (Laurichesse and Avérous 2014). Lignin is insoluble in water and is not hygroscopic in nature. It also tends to restrain dimensional changes that occur with moisture changes in the cell wall.

Figure 6 reveals the chemical structure of lignin. The linkage between polysaccharides and lignin as a lignin-polysaccharide complex is due to the links connecting lignin to the polyoses side groups of arabinose, galactose, and 4-O-methylglucoronic acid, as presented in Fig. 7. This sterically chemical structure of lignin reveals the difficulties of the complete separation of lignin from lignocellulosic materials (Li *et al.* 2015b).

A set of methods, such as thermal treatment followed by alkalline extraction, is normally employed to separate lignin from a lignocellulosic component. In order to achieve deconstruction of biomass material, the cementous thermal property of lignin needs to be removed.

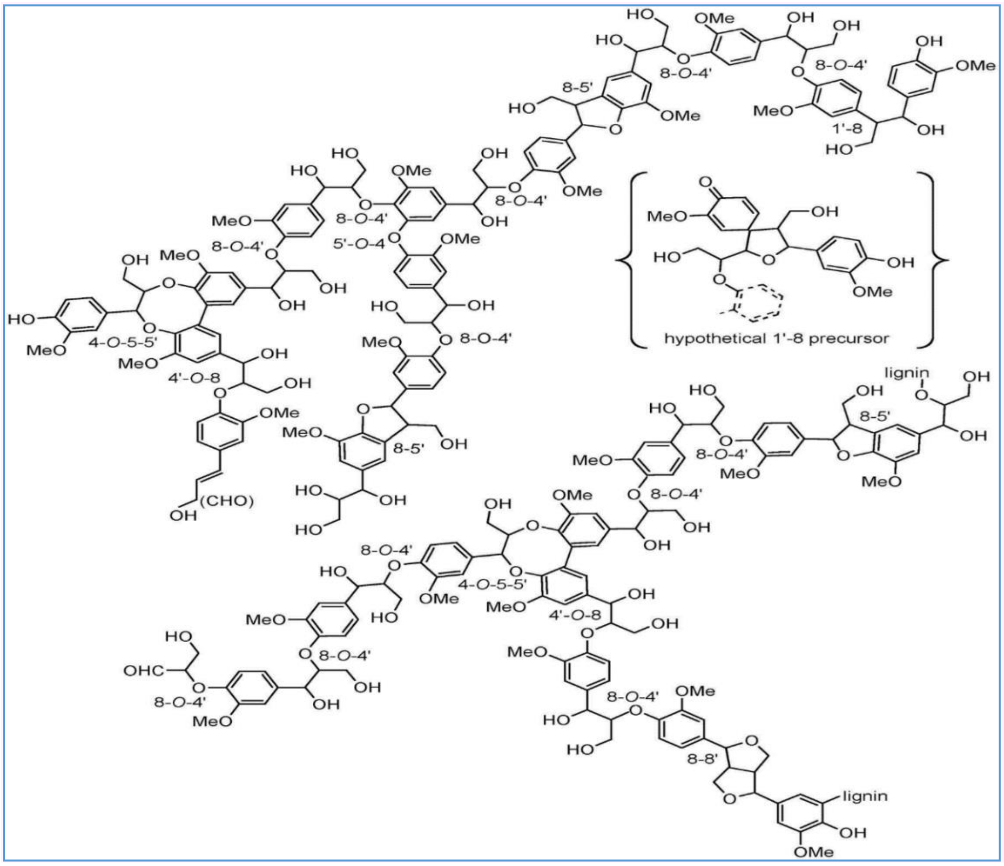


Fig. 6. Chemical structure of lignin, shown here as a contemporary model due to its complex structure (Reprinted from Kameshwar and Qin 2016)

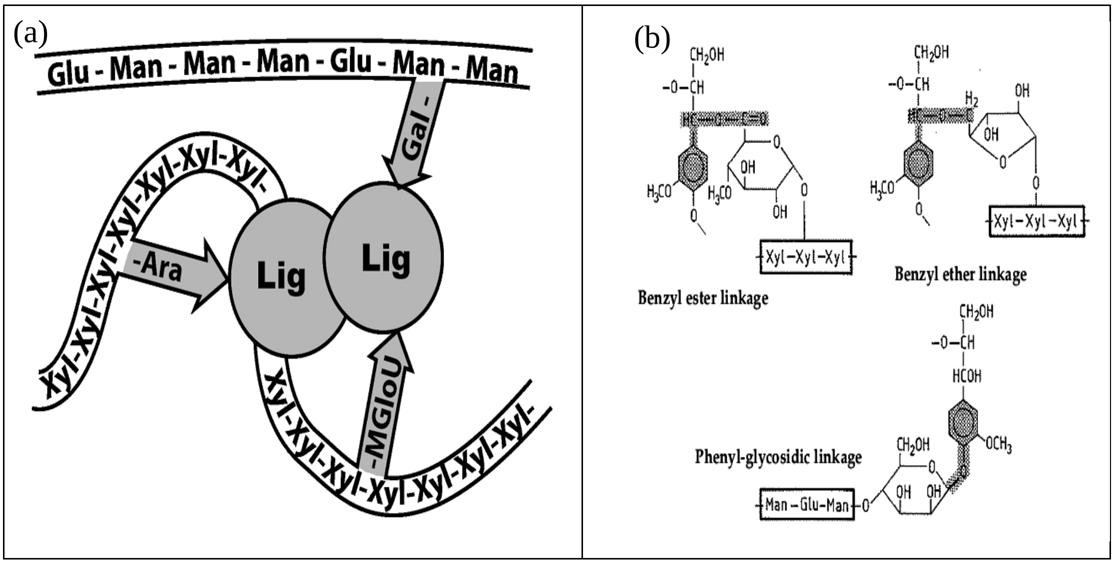


Fig. 7. Representation of: (a) schematic and (b) detailed representation of linkage for lignin and polysaccharides (Adapted from Fengel and Wegener 1983)

Starch

Starch is a carbohydrate in which the glucose units are joined together by glycosidic bonds. Generally, staple foods such as potatoes, maize (corn), wheat, rice, and cassava contains large quantity of starch (Patel *et al.* 2015). Organs and tissues containing starch granules include pollen, leaves, stems, woody tissues, roots, tubers, bulbs, rhizomes, fruits, flowers, and the pericarp, cotyledons, embryo, and endosperm of seeds (Nanda *et al.* 2015). Starch synthesis takes place during the development and maturation of storage organs, such as tubers, fruits, and seeds (Theng *et al.* 2015). There are two types of starch polymers, amylose, and amylopectin. These polymers exist in nature, most often with a composition of 10% to 30% and 70% to 90%, respectively (Aktin *et al.* 1988; Tawil *et al.* 2012). Amylose is a linear homopolymer of glucose with 1,4-α-glycosidic bond. Amylopectin is a highly branched starch polymer with linear linkage of 1,4-α-glycosidic bond, and its branch is formed by a 1, 6-α-glycosidic bond (Theng *et al.* 2015).

Physical properties of the two types of starch materials are presented in Table 3 (Preiss 2009). Starch is not only consumed as a food, but it is also built into various other industrial applications. Since the 1930s, carbohydrate chemists have developed numerous products that have greatly expanded starch use and utility, including waxy corn starch, high-amylose starch (primarily used by candy manufacturers due to its high-strength gels that give candy shape and integrity), chemically modified starch to gain appropriate texture, and in process food products to improve quality and shelf life (Mason 2009).

Table 3. Properties of Amylose and Amylopectin In Starch (Mason 2009)

Properties	Amylose	Amylopectin
General structure	Linear	Branched
Color with iodine	Dark blue	Purple
Average chain length (glucosyl units)	100 to 10,000	20 to 30
Degree of polymerization	100 to 10,000	10,000 to 100,000
Solubility in water	Variable	Soluble

Challenges on Glucose Production from Lignocellulosic Biomass

In principle, cellulose, hemicelluloses, and starch from lignocellulosic biomass can be utilized to produce glucose, though they require effective pretreatment processing to ensure high quality glucose production. Currently, the technologies involved in converting cellulose from polysaccharide sources are progressing and have yet to be commercially useful. There are still many challenges that need to be overcome before these technologies become commercially available. Wyman (2004) made cost comparisons for the production of ethanol from sugar crops, starch, and lignocellulosic material, including the energy balance for each process. They concluded that substantial research was needed to advance the technologies, with high attention focused on overcoming perceived risk and capital investment. The conversion of biomass into glucose is one of the main research interests in recent years, and much research has been conducted. The basic need of the process is still, however, to find an effective method to disrupt biomass integrity before it can be optimally utilized (Li *et al.* 2015b; Miran *et al.* 2016). Cumulative challenges include the reduction in cost for material collection (logistic), conversion process (high enzyme cost and high material cost for reactor construction), waste accumulation, and the optimization and process integration.

Pretreatment is one of the critical steps in biomass utilization, as it has high impact on downstream processes. It has been suggested that pretreatment contributes to approximately 18% of the total production cost of ethanol production. Pretreatment with dilute sulfuric acid has been the subject of research for more than two decades, particularly for work related to bioenergy research. It is reported that the dilute sulfuric acid helps to recover 80% to 90% hemicellulose in hot water extract after the pretreatment (Yang and Wyman 2008). The progress and challenges for the conversion of biomass into sugar are reviewed and summarized in Table 3.

Table 3. Summary of Major Research Areas, Progress, and Challenges for the Conversion of Biomass into Biofuels (Sainz 2009)

Area	Description	Progress	Challenges
Feedstock	Use and modification of biomass sources: agricultural, forestry or municipal waste, or dedicated energy crop	Initial analyses of feedstock yields and collection costs; compositional analyses; research into cell wall biosynthesis and chemistry	Reducing collection/feedstock costs; determination of desired feedstock characteristics; genetic modification of feedstock to maximize value
Pretreat-ment	Mechanical and chemical treatments to facilitate conversion of lignocellulosic biomass to fermentable sugars	Evaluation of effectiveness of different pretreatment processes on a variety of feedstock; characterization of inhibitors in downstream processes	Reducing capital expenses and input costs; reducing energy inputs; recycling/usage of waste streams; process integration
Enzymatic hydrolysis	Enzymatic conversion of cellulose and hemicelluloses polymers to fermentable sugars	Reduction in cost of cellulase enzymes; understanding of *T. reesei* and *A. niger* cellulases	High enzyme costs; poor activity/long incubation times; optimized enzyme mixtures for specific feedstock/processes
Fermen-tation	Conversion of fermentable sugars to ethanol or other fuels and bio-products	Characterization of C5/C6 sugar fermenting organisms; analysis of tolerance to inhibitors in fermentation	Organisms with rapid growth, improved tolerance to inhibitors and fermentation of multiple sugars under industrial conditions
Process engineering	Engineering designs to enable economic biomass processing at commercial scale	Process models constructed, tested, and revised	Optimized process integration; incorporating best (sometimes proprietary) data into models

Biorefinery Concept for the Glucose Production from Biomass

Several strategies have been employed in developing a competitive glucose manufacturing process utilizing biomass. One of the strategies was developed based on a novel biorefinery concept. The U. S. National Renewable Energy Laboratory (NREL) defines a biorefinery as “a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass” (NREL 2009). The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. NREL further explains that their biorefinery concept is built on two different “platforms”: first, the “sugar platform,” and, second, the “syngas platform,” which are based, respectively, on biochemical processes with a focus on sugar fermentation, and thermochemical processes with a focus on biomass gasification. The concept also has been extensively reviewed since the beginning of the first generation of biofuel, and has evolved into its current state of development with the second generation of biofuel. Detailed explanations for each process route have been presented in various publications and are summarized further in Fig. 8.

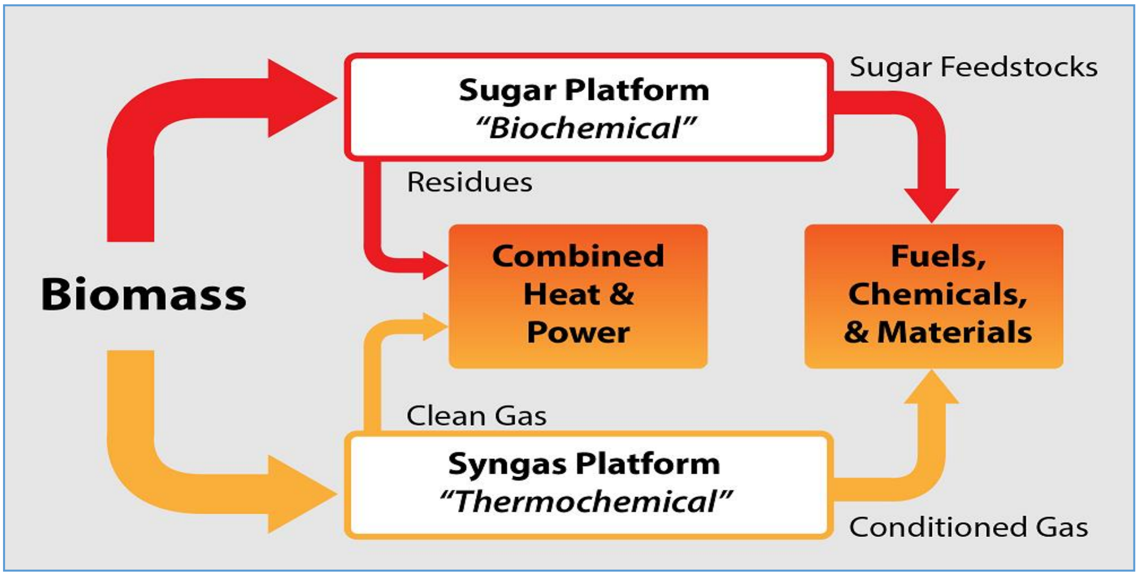


Fig. 8. Novel biorefinery concept with biomass as feedstock (National Renewable Energy Laboratory 2009)

The following general equations describe the conversion of biomass composition into several chemicals of interest (Crocker 2010),

$$\text{Lignocellulose} + H_2O \rightarrow \text{Cellulose} + \text{Hemicelluloses} + \text{Lignin} \ (+ \text{Starch}) \quad (1)$$

$$\text{Hemicelluloses} + H_2O \rightarrow \text{Xylose} \quad (2)$$

$$(C_5H_{10}O_5)_n + \text{Catalyst} + H_2O \rightarrow \text{Furfural}\ (C_5H_{10}O_5) + 3H_2O \quad (3)$$

$$\text{Cellulose}\ (C_6H_{11}O_6)_n + \text{Catalyst} + H_2O \rightarrow \text{Glucose}\ (C_6H_{11}O_6) \quad (4)$$

$$\text{Starch}\ (C_6H_{11}O_6)_n + \text{Catalyst} + H_2O \rightarrow \text{Glucose}\ (C_6H_{11}O_6) \quad (5)$$

where n > 10,000 units of glucose or other monosaccharide. The detailed glucose conversion process and its related products are further explained in Fig. 9.

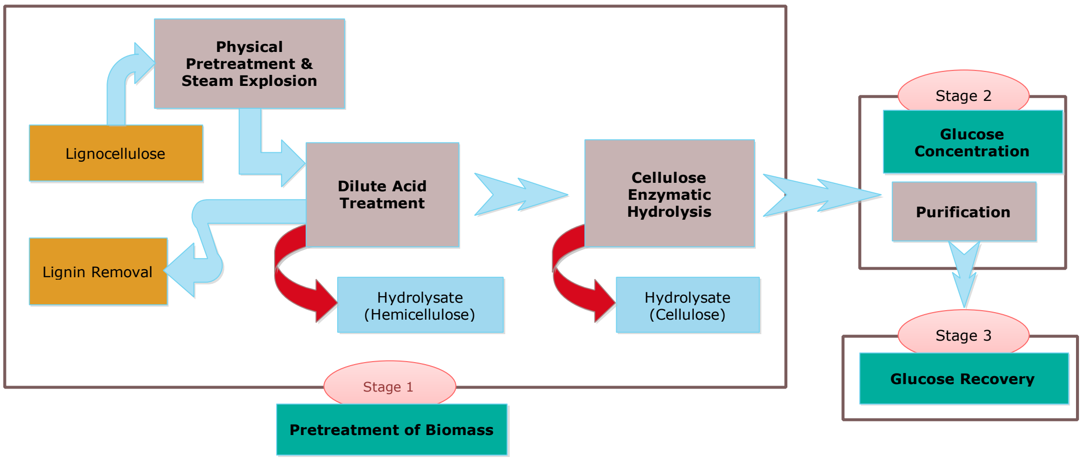


Fig. 9. Stages of the conversion of biomass materials into glucose (Adapted from Zaldivar *et al.* 2001)

The use of biomass for energy, fuel, and chemicals can be developed with the concept of biorefinery as described earlier. The stoichiometry reaction for sugar to ethanol can be expressed as,

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_5OH + 4CO_2 \qquad (6)$$

with sucrose as its source, and

$$C_6H_{12}O_6 + H_2O = 2C_2H_5OH + 2CO_2 \qquad (7)$$

with glucose as its source.

Other than ethanol, glucose also can be used as a precursor during the synthesis of other important products such as food and organic acid. Typically, this production needs the integration of various processes to fractionate biomass into various end-products. The thermal pretreatment and acid hydrolysis process initially combined the mechanical and thermal fractionation processes. Generally, there are three main stages of operation in biorefinery (Borole 2015):

a) The first step involves the size reduction of the materials; biomass will need to be cut to suitable size for effective thermal pretreatment. These operations may increase the overall available surface area for next operation due to the formation of internal microporous material. In this stage, thermal-treated material can be extracted and its components, such as lignin and hemicelluloses, also extracted. Cellulose may be transformed into individual components as suggested in the above general equations.

b) In the second stage, the individual component that was separated earlier may undergo several processes to separate it into its monomers. Several processes need to be employed at this stage, such as primary hydrolysis (acid or enzyme), followed by its secondary process, such as glucose fermentation into bioethanol.

c) The third stage involves the purification of the products of each individual product. If the desired final product is purified glucose, several steps such as the extraction of other intermediate of products including levulinic acid, furfural, and other acids (such as formic and acetic acid), take place at this stage.

Pretreatment of Lignocellulosic Biomass

Utilization of biomass for industrial applications has been of great interest since the beginning of industrialization. Due to its stability in its natural forms, it is difficult to utilize lignocellulosic biomass without pretreatment. Various works and reviews of the pretreatment of lignocellulosic materials have discussed a wide range of pretreatment methods. Factors related to the success of biomass utilization included the crystalline index of materials, the pore size of the internal structure to make it accessible to chemical or enzymatic reaction, and the content of lignin that binded together the biomass (Torget *et al.* 2000; Niu *et al.* 2016). Other success factors include a high surface area to immediately enable chemical reactions at the surface and also that the biomass is free from any toxic composition that may block enzyme accessibility (Saeman 1945; Oliva *et al.* 2006; Linde *et al.* 2007). The thermal-based pretreatment process was developed primarily for use with the fermentation process, due to some limitation of immediate biomass utilization with enzymatic hydrolysis (Gerssen-Gondelach *et al.* 2014). For example, Meng *et al.* (2013) reported that the biomass particle size might influence the enzymatic hydrolysis yield. The smaller particle size of biomass materials than the large paricle size of cellulase enzymes might enhances synergistic interaction and hence enzymatic hydrolysis yields (Soler-Illia *et al.* 2002). These examples show the main reason why pretreatment is required for successful biomass utilization.

Over the years, numerous methods have been proposed for the conversion of biomass materials into glucose. Initially, source materials need to be either mechanically chipped or milled to decrease their size to one suitable for feeding into pretreatment chambers (Saeman 1945; Diner *et al.* 2015). Once the material has been pre-treated with a thermal pretreatment process to increase the accessibility of its materials, it is ready for next process, *i.e.*, the hydrolysis process, through acid or enzymatic hydrolysis, to obtain glucose. By increasing the severity of pretreatment (such as through the combination of several process factors including time, high temperature, and pH) and varying the sources of raw materials, the species and concentration of fermentation inhibitors (such as acetic acid, furfural, and HMF) can vary greatly (Zaldivar *et al.* 2001). Fermentation inhibitors can be divided into several inhibitor sets depending on their sources, such as acetic acid coming from the breakdown of cellulose and hemicellulose (due to the de-acetylation of hemicellulose), furfural (due to thermal degradation of 5-carbon sugars), and 5-hydroxymethyl furfural (HMF, *i.e.* the degradation product of 6-carbon sugars) (Garrote *et al.* 2002). Other enzymatic inhibitors, such as levulinic or formic acid (due to extensive degradation of furfural and HMF), can be formed by increasing the process parameters. Additionally, chemicals with aldehyde groups such as 4-hydroxybenzaldehyde and phenols, including catechol and vanillin, can be formed from the available lignin fraction in the biomass sources (Oliva *et al.* 2006).

Hydrolysis and the degradation of glycosidic bonds in starch, cellulose, and hemicelluloses, can in general be represented as in Fig. 10. The presence of the reactive proton [H+] in the reaction solution leading to the fission of glycosidic bonds happens in three steps, and with two options. In the potential dominant pathway using Option 1 (route →), initially, the proton will interact rapidly with the glycosidic oxygen that links two unit glucose (Fig. 11, part I) to form acid conjugates (Fig. 10, part II). In the subsequent steps, C–O bonds will be slowly cleaved to form a cyclic carbonium cation (Fig. 10, part III). Option 2, the reaction of the left side, shows that protonation also occurs at the oxygen ring (Fig. 10, part II’), resulting in the opening of the ring and the formation of a non-cyclic carbonium cation (Fig. 10, part III’). It is not clear whether the cyclic or non-cyclic carbonium cation will occur until the final steps, when both cations will form a stable end-product of glucose with the release of the proton (Li *et al.* 2015a).

Hydrothermal Pretreatment

The pulp and paper industries were the first industries that utilized hydrothermal treatment to fractionate biomass such as cellulose and lignin. Most of the present hydrothermal biomass pretreatments originated from this industry, with improvements to suit the need of biomass and its processing (Ingram *et al.* 2011; Ullah *et al.* 2015; Wu *et al.* 2015). In the pulp and paper industries, feedstock is separated into two parts: an aqueous extract and a pulp for the making of paper. Aqueous extract is composed mainly of hemicellulose, lignin, and chemicals, which can be further purified. The aim of a thermal pretreatment for lignocellulosic biomass was to develop a moderate treatment condition to maximize the hemicelluloses yield, which was easily hydrolyzed through steam treatment (Wu *et al.* 2015). It seemed that with a simple treatment combining steam and water, the process could be regarded as environmentally friendly (Garrote *et al.* 1999). Additionally, hemicelluloses were recovered with good yields, and little byproduct was generated.

In specific cases, certain chemicals, such as levulinic acid and furfural, are the product of interest; for example, they are the desirable reaction intermediates in the production of liquid alkanes by chemical catalytic processing (Huber *et al.* 2006). For that particular requirement, the process will be developed specifically to obtain an optimum condition of specific products, such as levulinic acid, acetic acid, or only glucose. The mechanism for the formation of glucose from the starch, cellulose, and hemicelluloses can be represented by the following reaction mechanisms, as presented in Fig. 10.

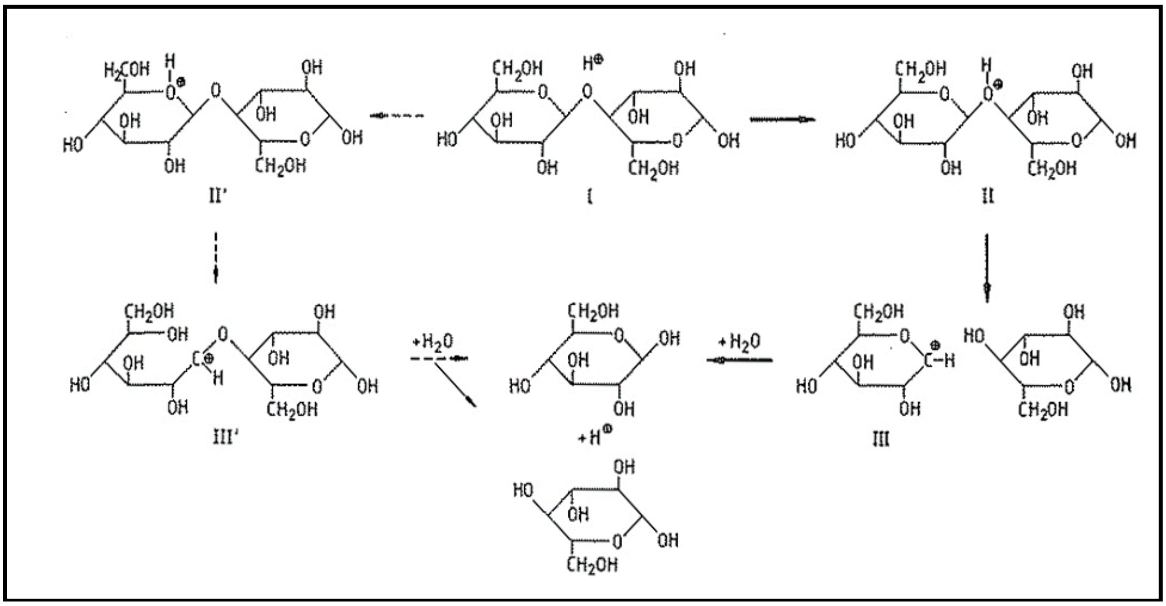


Fig. 10. Mechanism of acid hydrolysis of glycosidic bonds in starch, cellulose, and hemicellulose into monosaccharide (Adapted from Fengel and Wegener 1983)

In most of the present technology, two-stage processes are employed. In the first stage, biomass materials are pre-treated to break down ultra-cellular components and its cell wall structures (Chaturvedi and Verma 2013). The second step usually involves the depolymerization of polysaccharides to monosaccharides (Duan and Kasper 2011). In the second step of most of the present works, there is much interest to employ an enzymatic process involved with generating bioenergy. On the other hand, hydrolysis through the utilization of acid (either dilute or concentrated acid) has been found to be a simple process, and normally the starting point for most research on the conversion of biomass into glucose (Brodeur *et al.* 2011). The process has been found to give moderately high glucose yields in relatively short times compared to the enzymatic process. During dilute acid hydrolysis, a proton in acid, due to its size, is able to migrate to the glycosidic bonds of the cellulose, starch, and hemicellulose (Brodeur *et al.* 2011; Wu *et al.* 2015). With its size and due to its relatively very high reactivity during processing, it is difficult to limit the extended proton hydrolytic activity on polysaccharides and glucose. Most of the time, under extended hydrolysis condition, glucose undergoes further acid catalysis to form degradation products. The most common degradation products of glucose are furfural (xylose) and hydroxymethylfurfural (HMF) (Shi *et al.* 2012).

Both furfural and HMF form precipitates with residual insoluble polymers and are the main causes of reactor problems (Nabarlatz *et al.* 2005; Shi *et al.* 2012). The formation of precipitate has been linked to the increase in process temperature and turned into a source of yield reduction (Shi *et al.* 2012). Most hydrolysis processing for dilute acid has been done at more than 100 °C, while for concentrated acid, processing has been done at a temperature below 90 °C. For acid below 0.5 mol/L, the temperature usually is greater than 120 °C; if the temperature was approximately 90 °C, a concentrated strong acid >1.0 mol/L was required (Sun *et al.* 2009). The combination of high temperatures and strong mineral acids leads, however, to the faster corrosion of the reactor and to problems related to the degradation of sugar and accumulation of non-sugar by-products in the reactor.

Biomass materials usually consist of cellulose, hemicellulose, and lignin. These materials need to be separated by chemical solubility; lignin, for example, is soluble in alkaline solution, while hemicelluloses only need hot water for extraction. Some of chemicals produced during acid catalytic process, such as furfural, hydroxymethylfurfural (HMF), and levulinic acid, are desirable chemical intermediates for liquid alkene production (Huber *et al.* 2006; Sun *et al.* 2009), although they are undesirable chemicals for processes that depend on enzymes and microorganisms (Cara *et al.* 2008). Therefore, hydrolysate obtained during high severity treatment is usually not suitable for enzymatic and microorganism utilizations. A less severe thermal treatment does not, however, allow the complete disintegration of the cellulosic portion for optimum enzymatic utilization.

Acid-catalyzed cellulose hydrolysis is heterogeneous in nature and very much affected by the cellulose properties (*i.e.*, amorphous or crystalline) and material dimensions. Hydrolysis reaction rates are unaffected when using particles with dimensions 20 to 200 mesh; a uniform material size would optimize hydrolysis conditions (Kumar *et al.* 2009). In most cases, however, achieving the correct particle size would require high effort in the form of mechanical energy for debarking, cutting, and grinding from massive material to a powder-like material. These difficulties have made virgin solid biomass material the last choice in the processing or transforming biomass into sugar and ethanol.

Steam Explosion Pretreatment

Steam explosion is a thermomechanical pretreatment process. This pretreatment process allows breaking down the lignocellulosic structural components by the action of saturated steam heating, shearing forces and formation of organic acids during the process (Jacquet *et al.* 2015). Steam explosion is one of the popular biomass pretreatment processes based on the utilization of direct steam injection of biomass materials. Several pretreatment processes were developed based on this method, such as steam explosion and AFEX technology. Steam explosion technology was developed for hardboard production by W. H. Mason in 1925. Recently, the use of steam explosion has been extensively studied for the pretreatment of lignocellulosic materials due to its ability to hydrolyze glycosidic bonds in hemicelluloses, assist in the cleavage of lignin-hemicelluloses bonds, and increase the accessibility crystalline cellulose bonds towards acid and enzymatic hydrolysis (Kumar *et al.* 2009; Brodeur *et al.* 2011). Two types of steam explosion design have been tested at laboratory and pilot scale studies. The first type is through a batch process known as the Masonite Gun. The second type is based on the same batch principle, but also includes a continually-running feeding system called the Stake reactor (Zhang and Chen 2012; Jacquet *et al.* 2015). Both steam explosion systems have a vertical cylinder to be filled with wood chips or other type of biomass. They are sealed and injected with saturated steam with pressure up to 2.5 MPa. Materials inside of the reactor will be steam heated between 180 and 260 °C with processing time approximately 2 to 30 min depending on the type of biomass and its final application (Zhang and Chen 2012).

Steam explosion processing has been extensively studied with the aim to overcome three main factors for ultimate lignocellulosic material valorization: (1) the physical barriers due to the presence of lignin, (2) the crystallinity of cellulose, and (3) the physical access for acid and enzymatic reaction on lignocellulose materials (Kumar *et al.* 2009; Zhang and Chen 2012). The extraction and fractionation of lignocellulosic materials can be optimized once maximum bulk diffusion is achieved due to high numbers of individual lignocellulose fibers. Internal diffusion within the cell walls, on the other hand, is facilitated by the swelling of the structure through the introduction of chemical or through internally generated chemical resulting from autohydrolysis (Jacquet *et al.* 2015).

A work by Heitz *et al.* (1991) used the Stake II system for steam explosion pretreatment on *Populus tremuloides* to recover hemicellulose and lignin based on varying the severity of treatment on materials. Cellulose obtained from the processing was subjected to enzymatic hydrolysis. About 65% of hemicellulose and 80% of lignin were recovered from the process. Sugar hydrolysate obtained from enzymatic hydrolysis was also found suitable for fermentation into ethanol. Various other materials have been subjected to treatment with both systems, such as sugarcane bagasse, corncob (Nabarlatz *et al.* 2004), corn stalks, and almond shell (Nabarlatz *et al.* 2005). Various combinations, including with the addition of acids, alkali, peroxide, and gasses, were tested to find suitable parameters for the respective processes as well as to match them with products of interest (Nabarlatz *et al.* 2005). The steam explosion process has been extensively studied as a pretrement process, and reviewed, modeled, and applied (including optimization) for producing lignocellusic fiber (Crocker 2010; Jacquet *et al.* 2015; Bajpai 2016). The basis of the process is material in the form of chips subjected to direct high steam pressure, followed by a sudden decompression through an orifice towards atmospheric pressure (Linde *et al.* 2007).

This explosive discharge changes the starting solid cellulose materials into fibrous mulch, because the combination of mechanical and chemical actions on the materials cause materials to defibrillate, as depicted in

Fig. 11.

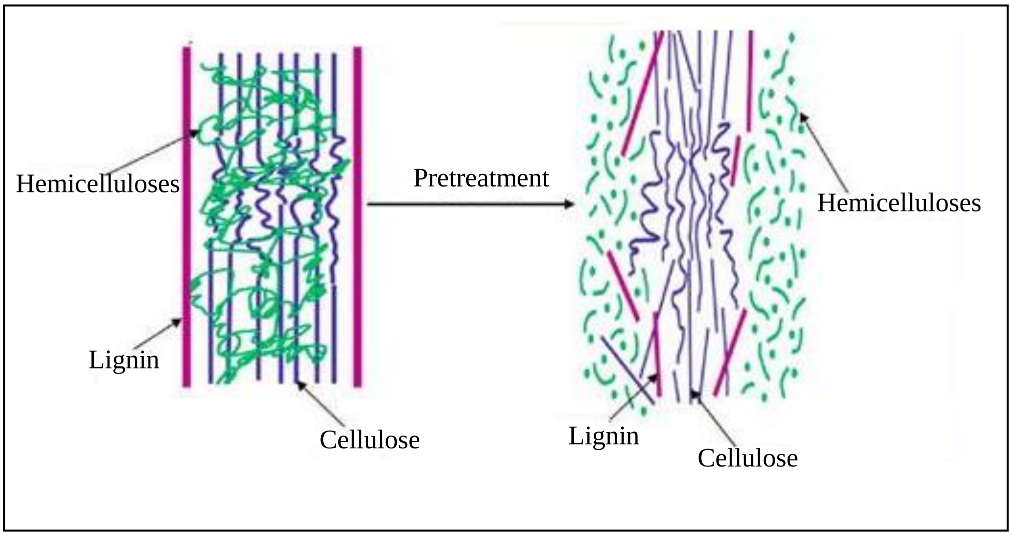


Fig. 11. Schematic of pretreatment goals on lignocellulosic material at higher severity treatments (Adapted from Hsu *et al*. 1980)

Steam-exploded materials can be treated with water and chemicals to isolate several of their interesting chemical components. For example, hemicellulose and lignin are immediate components that can be separated from steam-exploded materials by water and alkali extractions. The residue of an extraction process usually exists in the form of insoluble components that are high in cellulose and almost free of hemicellulose and lignin (Jacquet *et al.* 2015).

There are several setbacks of the steam explosion technology. The steam exploded biomass yield is typically quite low; it has been reported at approximately 78% and 58% at low severity and high severity, respectively (Zakzeski *et al.* 2010). This is due to the removal of hemicellulose and lignin together, with condensate produced during the heating of treated materials. Other drawbacks of steam explosion technology include the formation of pseudo-lignin due to the high temperature of the steam explosion, and that it requires the direct utilization of the treated material in the bioethanol conversion process (Zakzeski *et al.* 2010; Ioelovich 2015).

Autohydrolysis

Autohydrolysis is a hydrolytic process that takes place in a thermal-based process catalyzed by acids naturally formed from biomass chemical composition (such as acetic acid) or by adding other acids (mineral acid, organic acid) for the reaction to start (Lee *et al.* 2014; Jönsson and Martín 2016). Autohydrolysis normally happens in a thermal process. Thermal processing thus has become a basic requirement of the present biomass pretreatment technology, which utilizes both physical (high temperature and pressure) and chemical processes to achieve effective pretreatment. Autohydrolysis helps increase the surface accessibility for hydrolysis, promotes cellulose decrystallization together with partial starch and hemicelluloses depolymerization, and reduces the lignin-recalcitrant behaviors in the treated biomass (Lee *et al.* 2014).

During hydrothermal pretreatment, much of the hemicellulose is hydrolyzed and the byproducts remain in a steam condensate, while lignin can be depolymerized and will release some portion of its phenolic compound into condensate (Katahira *et al.* 2016). Most of the lignin will usually remain inside of the biomass system and can be removed with the addition of an alkaline solution after extraction. Acetic acid that was formed by acetyl groups in hemicellulose (through autohydrolysis) will further help to hydrolyze the beta-glycosidic linkage of hemicellulose and lignin. Depending on the source of biomass and the composition of hemicellulose, nearly 50% of the biomass (mainly the cellose portion) will be left as a solid residue after hydrothermal treatment (Katahira *et al.* 2016).

All native lignocellulose matrials are organized in fibrils. Separation of those fibrils will increase the accessibility of surface availability for enzymatic reaction. There are certain traits of pretreatments that are preferred, such as the ability to increase surface area, reduce size, remove certain inhibitor components, swell biomass matrix, and increase the amorphous percentage of cellulose. However, certain phenomena usually occur during the pretreatment and autohydrolysis of polysaccharides in thermal treatment, including the following (Larsson *et al.* 1999; Shevchnko *et al.* 2000):

a) At a higher temperature, the color of treated material becomes dark, which is suspected to be due to the degradation of lignin and extractives in the biomass.

b) Saturated steam will increase surface temperature and diffuse into a porous structure of biomass. Free acetyl and uronic acid groups from hemicellulose will be transformed into organic acids such as acetic acid and uronic acids.

c) Due to the presence of acids, the hydrolysis of the glycosidic bonds of the hemicelluloses chains occurs. Hemicelluloses glycosidic chains are the most readily attacked chains due to their amorphous structure and immediate availability for chemical reaction. Depolymerization of hemicellulose will form intermediate and low molecular weight oligomers, which have active side chains that enable it to react with water. This makes the oligomers become partially depolymerized, thus forming monomers.

d) The monosaccharides of hemicellulose usually can be easily dehydrated into furfural and hydroxymethylfurfural if exposed to acidic conditions and relatively high temperature. However, the rate of formation for the degradation of monosaccharides is usually slower than the rate of hemicelluloses depolymerization and its monosaccharide formations.

e) Lignin that is available on the surface is also hydrolyzed by acid. Plasticization of lignin to exceed its glass transition temperature will further disrupt lignin and hemicellulose in the middle cell wall layers. Lignin will form spherical particles due to its polymeric properties.

f) The intimate association of lignin and hemicellulose through bonding between benzyl ester and benzyl ether linkages will depolymerize lignin into soluble components in the aqueous solutions.

g) Furfural and other products that were formed by the degradation of hemicellulose will react with depolymerized lignin and generate products that behave like lignin, known as pseudo-lignin.

h) Cellulose, in particular at the surface and amorphous region, will also be hydrolyzed. Extended hydrolysis on glycosidic bonds will lower the degree of polymerization of cellulose.

DIC Technology

The DIC is a thermo-mechanical process, which induces materials within a short period of time by saturated steam heat with abrupt pressure drop from saturated steam pressure to vacuum (Allaf *et al.* 2013). Generally a DIC process causes autovaporization and instant cooling of materials, which allows the structure of materials to be more expanded, while DIC conditions of higher serverity may imply higher breaking of cells. DIC technology was first developed at the University Technology Compiegne in 1987, when solving a problem related to dried vegetable material that required immediate softening when placed in water (Allaf *et al.* 1992). Henceforth, the process was called *Détente Instantanée Contrôlée (DIC)*, or *Instant Controlled Pressure Drop*. In general, the DIC process involves heat treatment of a material inside the DIC reactor, then the abrupt release of pressure towards the vacuum. The typical DIC system diagram is shown in Fig. 12. The sudden pressure drop causes quick cooling of the treated material and massive evaporation of water from it (Louka *et al.* 2004). Thermal pretreatment regime for biomass material can be divided into three severity treatment classes: (1) High severity thermal treatment with steam pressure between 15 to 30 bars; (2) Medium severity thermal treatment with steam pressure between 10 to 15 bars; and (3) Low severity thermal treatment with steam pressure less than 10 bars (Louka *et al.* 2004).

DIC pretreatment falls under the category of thermal pretreatment. Even though DIC can be considered a low severity pretreatment regime, it is still expected to contribute some degradation products from glucose and hemicelluloses at treatment temperatures about 170 °C. To avoid producing degradation products, selection of the pretreatment process and its parameters used in the pretreatment and conversion of glucose are very important (Messaoudi *et al.* 2015). DIC pretreatment is also expected to give some chain reactions towards a cleavage of chemical bonding in starch and cellulose superstructure, which then result in the depolymerization into glucose and a polymer with a low degree of oligosaccharides. General outcomes based on the thermal pretreatment of biomass has been reported by several researchers related to the pretreatment and process involved in the thermal operations (Messaoudi *et al.* 2015; Sánchez-Valdepeñas *et al.* 2015; Smichi *et al.* 2015).

The basis of the DIC process is a thermomechanical process that requires some moisture level inside material to be treated. The process starts by subjecting the process materials inside the DIC reactor to a vacuum, followed by pressurization under steam, then rapid expansion towards a vacuum (vacuum of approximately 50 to 100 mbar, with rapid valve opening time of approximately 0.2 sec) (Smichi *et al.* 2015). Operating temperature inside the DIC reactor is usually about 170 °C, while treatment time during high steam pressure was in range from seconds to minutes. The limitation of the DIC system has been due to the supply of steam limited to a maximum of only 1.0 MPa. In order to increase the rate of the hydrolysis reaction, very dilute acid was added to the materials (Louka *et al.* 2004). This enabled the use of lower temperature and minimize the residence time. It was also important to ensure that the extended degradation could be controlled by immediately lowering the reaction temperature.

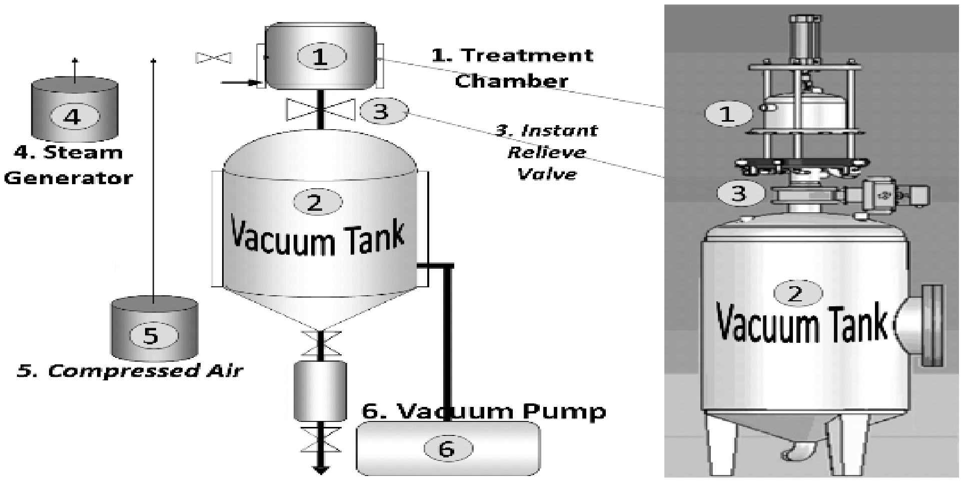


Fig. 12. Schematic diagram of DIC system

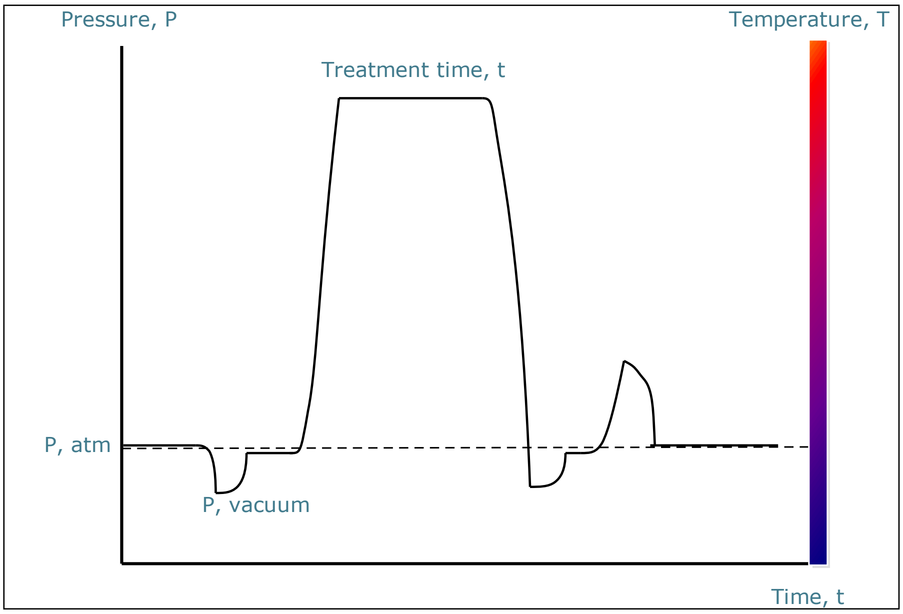


Fig. 13. Typical pressure-time profile for the DIC operating cycle

The rapid pressure drop ($\Delta P / \Delta t > 2.5x10^5\ Pa/s$) while the material is heated causes the bursting of moisture evaporation inside the bulk of material, which increases the potential to blow and break the cell walls' cavities (Louka *et al.* 2004). The degree of structural damage inside the materials depends strongly on the nature of the material as well as the parameters of the treatment. Processing material with the DIC process requires a certain level of moisture content in the subject material. Materials subjected to a vacuum will also undergo an auto-vaporization, also known as adiabatic cooling, which occurs instantaneously. The progress of the whole DIC process cycle is shown in Fig. 13. It has been very effective in several industrial fields such as microbiological decontamination, drying and texturing of biological products, and the extraction of volatile compounds and essential oils (Louka *et al.* 2004; Sánchez-Valdepeñas *et al.* 2015).

Various research and applications based on the DIC process have been performed since the inception of this concept, such as research on the structure expansion of fruit and vegetables (Louka *et al.* 2004), the pretreatment process for bioethanol production (Messaoudi *et al.* 2015; Sánchez-Valdepeñas *et al.* 2015), the enhancement of the extraction of essential oils (Besombes *et al.* 2010), and the sterilization and preservation of food materials (Nosyk *et al.* 2008). The study of non-isothermal regions and the determination of heat transfer coefficients for both DIC and dilute acid hydrolysis was performed to assist in understanding the thermal process on the obtained products. This understanding was important in order to control the degradation that could occur during the hydrolysis process. The DIC system was shown to have a high-heat transfer coefficient of approximately 45 to 80 times higher than the dilute acid hydrolysis process (Messaoudi *et al.* 2015). Subsequently, the glucose rate generation was approximately six times higher in the DIC system when compared to dilute acid hydrolysis. The higher glucose generation in DIC technology is due to the relatively higher rate polysaccharides conversion into glucose with the high rate of heat transfer (Louka *et al.* 2004).

Autohydrolysis with DIC Technology on Biomass Pretreatment

The efficient cleavage of targeted chemical links (alpha and beta bonds in polysaccharides) is a major goal in the conversion of lignocellulosic biomass. Several pretreatment methods have been studied to disrupt the cell wall structure of lignocellulosic biomass. The main aim of the physical pretreatments processes (*e.g.*, chipping, grinding, milling) is to break cellulose's crystallinity and reduce the polymerization degree of cellulose (Taherzadeh and Karimi 2008). However, physical pretreatment processes are only economically feasible in a large scale production. The biological process is viewed as an inexpensive and environmentally friendly pretreatment process for lignocellulosic biomass, but the lower hydrolysis yield compared to the other pretreatment processes makes it an unsuitable pretreatment process for lignocellulosic biomass (Wi *et al.* 2015).

Chemical pretreatments using concentrated acid and dilute acid are less attractive pretreatment processes for lignocellulsic biomass because they produce inhibitory molecules that can cause corrosion problems on the equipment, and may limit enzymatic hydrolysis and fermentation (Maurya *et al.* 2015).

Alkaline pretreatments using sodium, potassium, calcium, and ammonium hydroxides are effective in increasing cellulose digestibility and dissolving lignin (Chaturvedi and Verma 2013). The alkali conversion into irrecoverable salts during biomass pretreatment reaction is, however, a challenge for the alkaline approach. Among the various physicochemical and hydrothermal methods, steam explosion is the most widely utilized method in biomass pretreatment. Steam explosion pretreatment process, however, requires high energy consumption because it uses high temperature (between 200 and 250 °C) and pressure (up to 3 MPa) (Kumar *et al.* 2009). Moreover, this pretreatment process leads to the thermal degradation of sugars that inhibits microorganism growth and ethanol production. Conversely, autohydrolysis can treat lignocellulosic biomass at a comparatively lower temperature than steam expolision (Kumar *et al.* 2009). Autohydrolysis is an environmentally friendly pretreatment process for lignocellulosic biomass because it does not require additional chemicals or catalysts (Amendola *et al.* 2012). Autohydrolysis pretreatment may convert hemicelluloses into high yield soluble saccharides while rendering cellulose a rich, extractable solid residue (Amendola *et al.* 2012). Autohydrolysis pretreatment of biomass may, however, cause hemicelluloses degradation due to its high temperature (between 170 and 210 °C) (Hendriks and Zeeman 2009). Thus, it is urgent to define pretreatment process for lignocellulosic biomass that is economical and suitable for large scale operation.

An effective utilization of lignocellulosic biomass toward biofuel production may contribute greenhouse gas reduction. However, numerous problems associated with the practical utilization of these materials have not yet been solved. The available surface area of the lignocellusic biomass may further limit the future exploitation of pretreated materials (Wi *et al.* 2015). Thus, the selection of a superior pretreatment process strictly depends on the downstream utilization of the already treated fraction of lignocellulosic biomass (Ahmad and Qazi 2014). To overcome the disadvantages of existing pretreatment processes, studies suggest the usefulness of the combination process, which may lead to optimal fractions of the lignocellusic biomass components.

There has been an increasing demand for new pretreatment technique for getting higher yields with shorter pretreatment time (Akhtar *et al.* 2016). In recent years, instant controlled pressure drop (DIC) process has been indentified as potential and innovative process in various fields including drying (Mounir *et al*. 2011), extraction of volatile compounds (Besombes *et al*. 2010), decontamination (Allaf *et al.* 2011), texturing (Ben Haj Said *et al.* 2015), and pre-treatment for extraction of non-volatile molecules such as flavonoids (Allaf *et al*. 2013) and essential oil (Besombes *et al.* 2010). Mounir *et al.* (2014) applied a DIC process in expended granule powder into swelled- granule powder for intensifying solvent extraction. The study reported that the DIC pretreatment is an effective intensification process to increase diffusivity and accessibility, which made the grinding easier with expended granule powder. Mkaour *et al.* (2015) utilized DIC technology as pretreatment process for the extraction phenolic compound from olive leaves. The study reveals that DIC treatment changes the structure of the olive leaves with the destruction of cell walls. Mounir *et al.* (2011) examined the uniqueness of the DIC process and observed the abrupt pressure drop (P/t > 0.5 MPa/s) into a vacuum (about 5 kPa) in a short-time at controlled saturated steam pressure. Messaoudi *et al.* (2015) obtained higher amount of ethanol from DIC pretreated lignocellulosic wastes by enzymatic saccharification, when compared with the steam exploded wheat starw. However, the study argued that the higher amount of yield with DIC pretreated lignocellusic wastes might due to the lower severity of DIC pretreatment process. Slininger *et al.* (2009) reported that sugar may release from lignocellulsic biomass at a high severity pretreatment such as high acid concentration and high temperature. Similarly, Oliva *et al.* (2006) observed that, the xylose degrades into furfural and 5- hydroxymethylfurfural froms from hexose degradation such as mannose, galactose and glucose at high temperature and pressure.

It can be concluded that DIC technology is an efficient pretreatment process, which could be applied to treat lignocellulosic biomass for glucose and other biofuels. Sarip *et al.* (2011) observed that the DIC pretreated sago pith waste at 170 °C minimizes the glucose auto-degradation into fermentation inhibitors. Further, it was observed that the biomass impregnation with low acid concentration enhances the cellulose auto-hydrolysis. In light of all above, it can be recommended to carry out autohydrolysis of lignocellusic biomass followed by the instant pressure method of DIC technology. This recommendation is given because of both technologies having comparable characteristics in terms of pressure and temperature. The autohydrolysis pretreatment of raw lignocellulosic materials followed by DIC method would be conducted using saturated steam pressure at high temperature (up to 170 °C) for a short time (a few seconds to few mins), followed by an abrupt pressure drop as indicated in Fig. 13. This combination process would involve a heat treatment of materials inside the reactor, followed by the abrupt release of pressure toward the vacuum pressure (about 5 kPa). The sudden pressure drop causes a rapid cooling of the treated material. The auto-evaporation of the water during autohydrolysis may protect the thermal degradation of the hexose, and thus the resulting biomass expansion and texture change would help break cell walls and make the biomass components easily accessible.

CONCLUSIONS

1. Lignocellulosic biomass materials can be utilized as an alternative source for biofuel production.
2. Cellulose, hemicellulose, and starch from lignocellulosic biomass can be utilized to produce glucose, and require effective pretreatment processing to ensure high quality glucose production. Due to its stability in its natural forms, it is difficult to utilize lignocellulosic biomass without pretreatment.
3. Factors that influence the biomass pretreatment process are the crystalline index of materials, the pore size of the internal structure, and the content of lignin.
4. Numerous pretreatment processes have been proposed for the conversion of biomass materials into glucose. Most of the present technology utilizes two-stage processes; in the first stage, biomass materials are pre-treated to break down ultra-cellular components and its cell walls structures. The second step usually involves the depolymerization of polysaccharides to monosaccharides.
5. Autohydrolysis normally occurs in a thermal process, utilizing both physical (high temperature and pressure) and chemical combinations to achieve effective pretreatment.
6. Autohydrolysis helps to increase the surface accessibility for promoting cellulose decrystallization together with partial starch and hemicelluloses depolymerization, and reducing the lignin recalcitrance behaviors in the treated biomass.

7. DIC is a thermomechanical process that requires some moisture level inside the treated material. The process starts by subjecting process materials inside the DIC reactor to a vacuum, followed by pressurization under steam, then rapid expansion towards the vacuum (vacuum of approximately 50 to 100 mbar, with the rapid valve opening time of approximately 0.2 second).
8. A successful pretreatment process for lignocellulosic biomass implies the effective separation of the components and their successive exploitation. Thus, the selection of a superior pretreatment process strictly depends on the downstream utilization of the already pretreated fraction of lignocellulosic biomass.

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