BIOETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS BY ENVIRONMENT-FRIENDLY PRETREATMENT METHODS: A REVIEW

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Abstract. Lignocellulosic biomass is one of the abundant renewable bioresources on earth. Its chemical composition, i.e., lignin hinders ethanol production and commercialization. Pretreatment processes are vital for efficient separation of the complex interlinked components and enhance the availability of every component, i.e., cellulose and hemicellulose. However, for the bioethanol production, a major barrier is the removal of strong lignin component which is highly resistant to solubilization and a major inhibitor for hydrolysis of cellulose and hemicellulose. Pretreatment of biomass is necessary to make it susceptible to microorganisms, enzymes, and pathogens. Consequently, for the ethanol production, pretreatment of lignocellulosic biomass process is very costly. The initial pretreatment approaches include physical, physicochemical and biological methods. It found out that; pretreatment methods have a significant impact on efficient production of ethanol from biomass. However, extensive research is still necessary for the development of new and more efficient pretreatment processes for conversion of lignocellulosic biomass to ethanol. Present review article presents recent development on lignocellulose biomass pretreatment. We discussed the different pretreatment methods along advantages, disadvantages, and challenges for bioethanol production. This review includes benefits and drawbacks and chemical, physical, physiochemical and biological pretreatment along with existing problems. For the production of ethanol, this review will help researchers regarding selection, development and further planning of pretreatment for different lignocellulosic residues.

Keywords: *Asia, crop residue, cellulose, energy resource, environmental safety, hemicellulose, lignin*

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Introduction

Lignocellulosic biomass is one of the most suitable alternative energy sources which can be harnessed to meet up the challenges of energy security. Biomass has been a significant contributor in achieving sustainable development goals (Triwahyuni et al., 2015). Over the last few decades, researchers have thoroughly practiced multiple techniques to generate energy from biomass and its related materials (Ravindran et al., 2015; Yadav et al., 2017; Zhang et al., 2015). This achievement can be attributed to the main reasons like low cost and abundance e.g. ethanol production (Ruiz et al., 2013). Biodiesel is an energy conversion product made from animal fat and vegetable oil through the trans-esterification process. Several researchers have used plants and their products to generate energy such as rubber seed (Jose et al., 2011), Rubber seed oil (Dhawane et al., 2017), oil palm biomass (Bhatia et al., 2017), Wilson's Dogwood (Li et al., 2017), *Brassica napus* seed oil (Anwar et al., 2017), *Koelreuteria integrifolia* oil (Zhang et al., 2017), jatropha oil (Nisar et al., 2017), castor oil (Baskar and Soumiya, 2016), *Eruca sativa* (Mumtaz et al., 2016) and Pongamia biodiesel as fuel (Perumal and Ilangkumaran, 2017). But, the production of bio-diesel from lignocellulosic biomass is not suitable due to low oil contents. Several issues are involved in biomass gasification of the plant for operation and designing reasons. Most of these causes may end in malfunctioning of the plant (Ruiz et al., 2013).

In EU, the target has been set to replace 10% for their automobile fuel with biofuels by 2020 (Porzio et al., 2012). It has been unanimously planned to consume 93.67 10^6 USD to support 2nd generation biofuels on industrial demo schemes through seventh framework program (Balan et al., 2013). The United States is targeting to produce 60.5 10^9L of 2nd generation bio-ethanol by the year of 2022 (Langholtz et al., 2012). By 2020, China is also planning to consume 12.7 10^9 L non-grain fuel ethanol (Chang et al., 2012). India has also announced a goal to replace 20% fossil fuel consumption with bioethanol and biodiesel by this year (Ravindranath et al., 2011).

In Pakistan, Sugar Mills Association (PSMA) is the agency responsible for producing bioethanol in the country. (Asif, 2009) The industry is entirely dependent upon fermentation of sugarcane molasses. Currently, 21 distilleries are trying to produce different grade ethanol in the country with an annual capacity of 50010^6 L. One kg of molasses is estimated to yield 0.240-0.270 L ethanol depending upon the molasses quality. In 2011-2012, Pakistan generated revenue of 26010^6 USD from 46010^6 L ethanol export at the trading price of 0.65 USD/L (Bhutto et al., 2015). Production of ethanol from molasses is not a feasible strategy due to increasing molasses cost (Arshad et al., 2008). The decline in agricultural land for sugarcane cultivation is also a chief reason of sugarcane shortage in future (Bhutto et al., 2015). In future, this will decrease the bioethanol production in the country, so it is essential for Pakistan to diversify its ethanol production to attain the national ethanol requirement and foreign export. For bioethanol production, biomass in the form of crop residues such as wheat straw, rice straw, maize stalk, cotton stalk and sugarcane tops, etc. are available in Pakistan (*Table 1*) (Yasin, 2012).

Pakistan produces field-based crop residue (69 million tons per year) which are commonly considered useless. It is estimated that four major crops produce 50 million tons of residue annually including 6.88 million tons of sugarcane bagasse. It is estimated that 10.942 million tons resource potential is available from four crops (wheat, rice, corn and cotton) without commercial and domestic consumption (*Table 2*) (Mirza et al., 2017). Bhutto et al. (2015) forecasted five lignocellulosic feedstocks such as cotton straws, sugarcane tops, rice straw, maize stalks and wheat straw yearly yield from 2013-2030 in Pakistan (*Fig. 1*). They also predicted the increasing potential to produce 2nd generation bioethanol up to 11.897 109 L by 2030 *(Fig. 2*) (Bhutto et al., 2015). This review critically appraises chemical, physical, physiochemical and biological pretreatment methods for bioethanol production. This review will be helpful for researchers in selecting, developing and planning for pretreatment strategies related to the different lignocellulosic residue.

Table 1. *Seasonal available different crop residue in Pakistan (Yasin, 2012)*

Residue Availability	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**
Wheat Residue			■	■	■	■	■					
Rice Residue	■	■	■	■					■	■	■	■
Sugarcane top	■	■	■	■							■	■
Cotton stalk	■	■									■	■
Corn stalk		■	■				■	■	■	■		

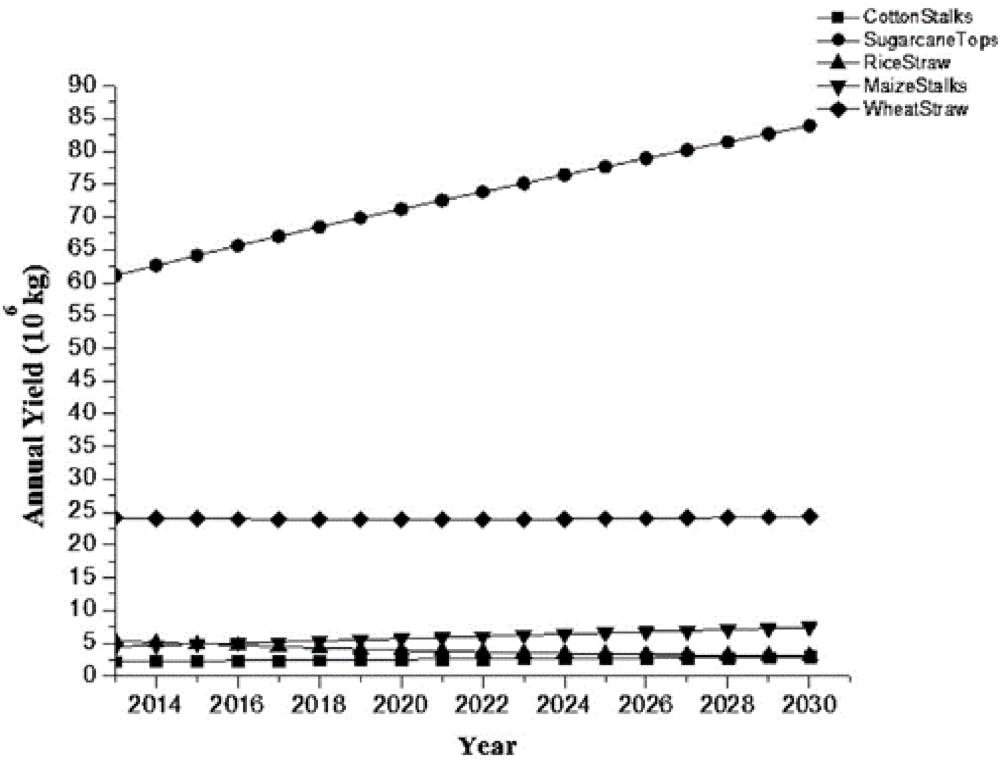

Figure 1. *Feedstock's potential from 2013-2030 based upon the available of crop residue such as wheat straw, rice straw, sugarcane tops, cotton stalks, and maize stalks and in Pakistan (Bhutto et al., 2015)*

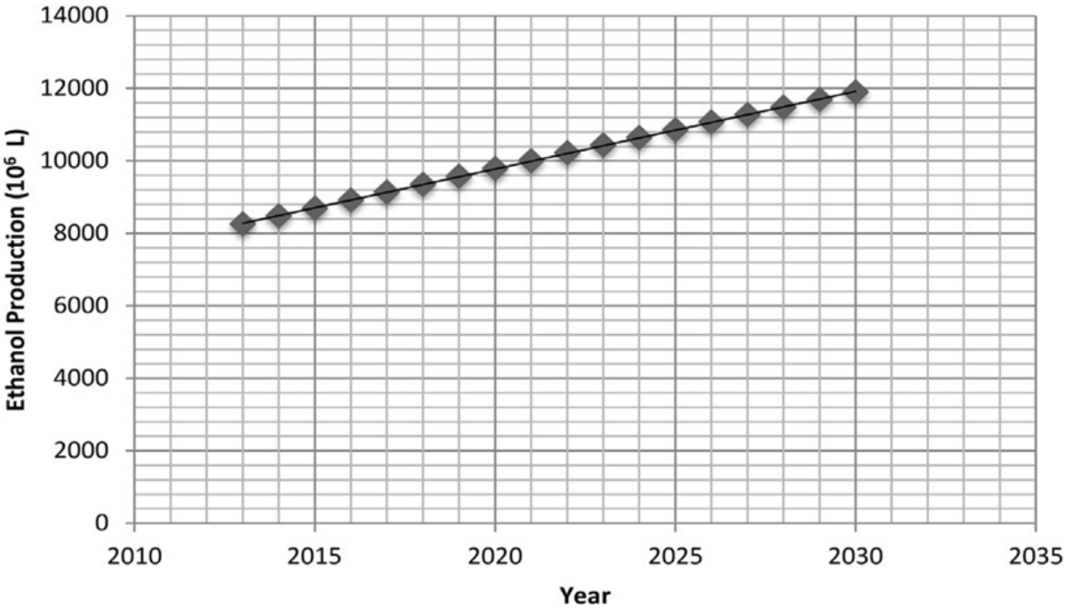

Figure 2. *Ethanol production potential from 2013-2030 based upon the available of crop residues such as wheat straw, rice straw, sugarcane tops, cotton stalks, and maize stalks and in Pakistan (Bhutto et al., 2015)*

Table 2. *Market price of different crops residue and ethanol potential after various pretreatment in Pakistan*

Lignocellulosic residue	Purchase price USD/10^3 kg	Treatment	Ethanol recovery	References
Wheat straw	25-35	H_2SO_4	19 g/l	(Bhutto et al., 2015; Saha et al., 2005a, 2005b)
Rice Straw	24	Dilute H_2SO_4	6.5–11.35 g/l	(Bhutto et al., 2015; Karimi et al., 2006)
Corn stalk	20	H_2SO_4	196 kg/t	(Bhutto et al., 2015; Demirbaş, 2004)
Sugarcane tops	8.5	H_2SO_4	3.35 g/l	(Bhutto et al., 2015; Dawson and Boopathy, 2007)
Cotton stalks	20	H_2SO_4	14.2 g/l	(Bhutto et al., 2015; Yu and Zhang, 2004)

Lignocelluloses

Lignocellulosic biomass refers to dry matter of plant (Collard and Blin, 2014) mainly composed of 25–30% hemicellulose, 40–50% cellulose, 15–20% lignin, and traces of pectin, nitrogen compounds, and inorganic ingredients (*Fig. 3*) (*Table 3*) (Knauf and Moniruzzaman, 2004; Mori et al., 2015). Cellulose is a linear syndiotactic (alternate spatial arrangement of side chain) polymer of glucose linked together by β-l,4-glycosidic bonds. Cellulose is the most abundant compound present on the earth with important features like biocompatibility, stereoregularity and hydrophobicity. Its distinct polymer chains have highly crystalline structure, and orderly bundled arrangements cause its stable properties. Its structure determines the framework of the cell wall. Lignin inhibits the process of hydrolysis because it is a complex hydrophobic polymer. Lignin is 3-D heterogeneous polycrystalline reticulated polymer which belongs to the polyphenol compound. This kind of polymers composed of phenylpropane structural units via ether linkages and carbon-carbon bonds. It has no proper regularity and orderliness of the repeating units. Hemicellulose is a mixture consists of different polysaccharides. Polysaccharides in hemicellulose are straight and branched as well. This polysaccharide has a low degree of polymerization, and without crystalline regions, so it can be easily degraded into monosaccharides such as fructose, xylose, galactose, dextrose, arabinose, and mannose (Balat, 2011; Chundawat et al., 2011; Karimi and Taherzadeh, 2016). Different factors determine the cell wall stability and extent of difficulty for its degradation. These factors include high crystallization zone along with several binding forces presents between cell wall constituents. The level of polymerization is also crucial in assessing wall degradation. The degradation of any class of ingredients will be subjected to the constraint of other ingredients. Thus, it is compulsory to degrade the network structure of lignin and efficient utilization of cellulose, lignocellulose by pretreatment. (Behera et al., 2014; Chaula et al., 2014; Liggenstoffer et al., 2014). Lignocellulosic biomass chemical structure causes key challenges to development and commercialization for ethanol because lignin surrounds the hemicellulose and cellulose. Pretreatment of biomass is necessary to make the biomass susceptible to microorganisms, enzymes, and pathogens. Consequently, for the bioethanol production, pretreatment of lignocellulosic biomass process is very expensive (Studer et al., 2011) (Mupondwa et al., 2016). Hence, for the selection of suitable pretreatment method should cover following points; the selected method should preserve the hemicellulose fraction; avoid the size reduction of biomass particles; reduce the energy demands; minimise the formation of degradation products; contain cheap catalyst recycle; contain cheap catalyst for pretreatment; and high-value co-product should produce from lignin (Wyman, 1999).

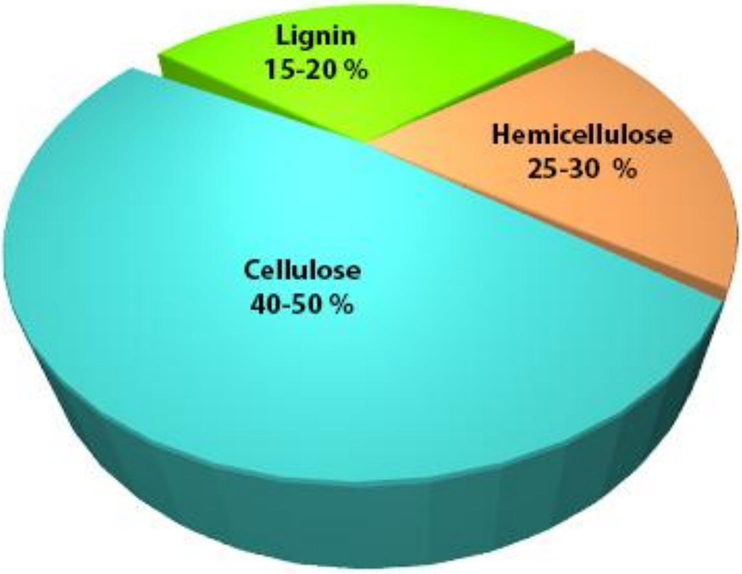

Figure 3. *General composition of lignocellulosic biomass*

Table 3. *Composition of various lignocellulosic biomass*

Agricultural and herbaceous biomass	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Ash (%)	References
Wheat straw	17–19	26–32	33–38	3.74	(Rabemanolontsoa and Saka, 2013; Saini et al., 2015)
Rice straw	12–14	23–28	28–36	19.8	(Qu et al., 2011; Saini et al., 2015)
Barley straw	14–19	27–38	31–45	-	(Saini et al., 2015)
Rye straw	16–19	27–30	33–35	-	(Sánchez, 2009)
Oat straw	16–19	27–38	31–37	-	(Sánchez, 2009)
Rice husk	26–31	18–21	25–35	17.27	(Ludueña et al., 2011; Rabemanolontsoa and Saka, 2013)
Sugarcane bagasse	20–42	19–25	42–48	-	(Kim and Day, 2011; Saini et al., 2015)
Sweet sorghum bagasse	14–21	18–27	34–45	-	(Saini et al., 2015)
Corn stover	7–19	24–26	38–40	6.8	(Qu et al., 2011; Saini et al., 2015; Zhu et al., 2005)
Corn cobs	14–15	35–39	42–45	3.53	(Kuhad and Singh, 1993; Prasad et al., 2007; Rabemanolontsoa and Saka, 2013)
Corn leaves	15.18	13.27	26.93	10.95	(Rabemanolontsoa and Saka, 2013)
Bamboo	20.81	19.49	39.80	1.21	(Rabemanolontsoa and Saka, 2013)
Switchgrass	10–40	30–50	5–20	5-6	(Lynel et al., 1999; McKendry, 2002)
Hazelnut shell	42.1	28.2	25.2	1.4	(Demirbaş, 2005)
Miscanthus	24–25	18–24	38–40	5.5	(Brosse et al., 2010; Rabemanolontsoa and Saka, 2013)
Hardwood biomass					
Beech	20	33	45	0.2	(Di Blasi et al., 2010)
Poplar	20	24	49	1	(Di Blasi et al., 2010)
Aspen	19.5	21.7	52.7	0.3	(Taherzadeh et al., 1997)
Cherry wood	18	29	46	0.5	(Di Blasi et al., 2010)
Willow	29.3	16.7	41.7	2.5	(Taherzadeh et al., 1997)
softwood biomass					
Pine	27.3	20.3	46.9	0.3	(Taherzadeh et al., 1997)
P.armandii Franch	24.1	17.8	48.4	0.2	(Wang et al., 2016)
Spruce	27.6	29.4	43.0	0.6	(Demirbaş, 2005)
Japanese cedar	33.8	23.1	38.6	0.3	(Rabemanolontsoa and Saka, 2013)
Fir	30	22	45	0.5	(Di Blasi et al., 2010)

Pretreatment techniques of lignocellulosic biomass

The main aim of pretreatment method is to change the chemical composition, macrostructure and microstructure of lignocellulose. It also makes the natural lignocellulosic macromolecule susceptible to microbial degradation (*Fig. 4*) (An et al., 2015). Hence, a pretreatment process is necessary to decrease the cellulose crystallinity, remove lignin and enhance the porosity of the material. An effective pretreatment should be cost-effective, produce fewer inhibitors and produce significant percent of cellulose support (Sun and Cheng, 2002).

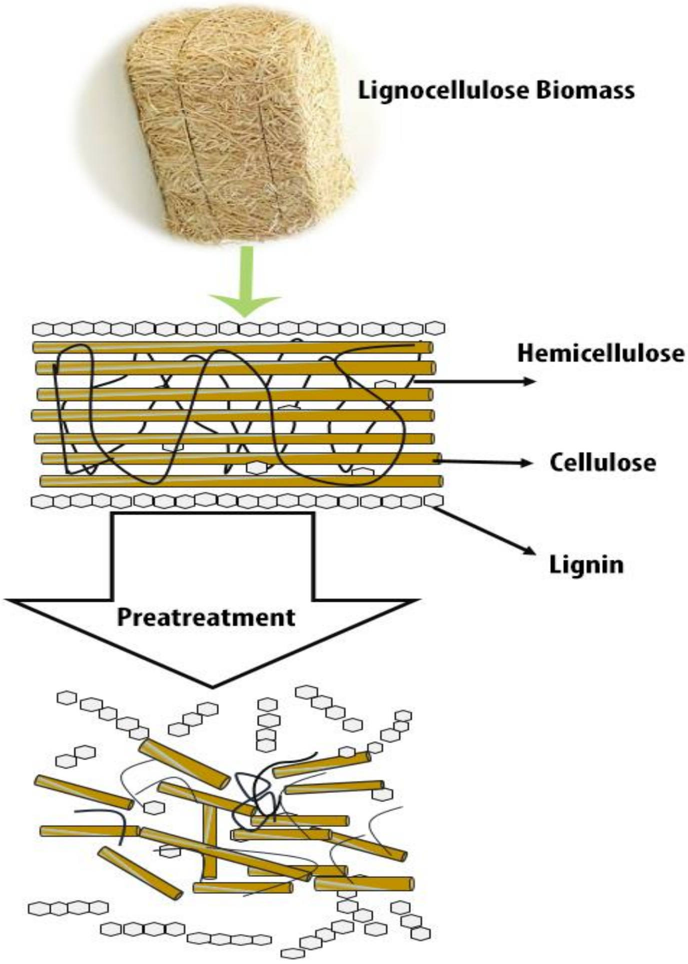

Figure 4. *Lignocellulosic biomass after pretreatment*

Common physical, chemical and biological methods or their combination are involved in this process (*Fig. 5*) (Taherzadeh and Karimi, 2008). Mostly physical pretreatment process include the biomass size reduction to increase the available surface area and reduce the cellulose crystallinity or degree of polymerization (Sanchez and Cardona, 2008). In chemical pretreatment process, various chemicals including acids are used for biomass pretreatment e.g. ionic liquids, an organic solvent, alkali and oxidizing agents (Fu et al., 2010; Fu and Mazza, 2011a, 2011b). Physio-chemical pretreatment is the combination of mechanical and chemical processes. The verity of methods contains catalyzed steam explosion such as carbon

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dioxide, ammonia fiber expansion, sulfur dioxide explosion, ammonia recycle percolation and liquid hot water (Sun and Cheng, 2002). In biological pretreatment, natural microorganisms (e.g. bacteria, soft-rot and brown-white fungi) having enzymes are used to destruct the cell wall of lignocellulosic biomass (Sánchez, 2009). Chemical and physical pretreatment have relatively good results as compared to other pretreatment, but apparatus requirement is very strict and causes severe pollution. Biological pretreatment process is environment-friendly and consumes less energy as compared to other pretreatment methods. However, biological pretreatment is expensive and enzymes activity during biomass decomposition is very slow requiring long duration (Taherzadeh and Karimi, 2008).

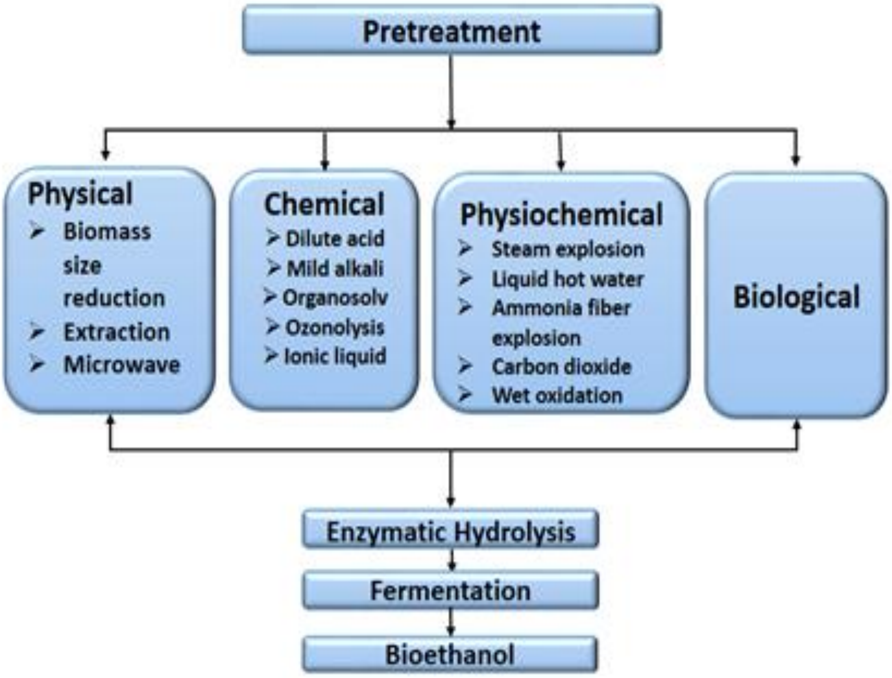

Figure 5. *Various types of pretreatment methods*

Physical pretreatment

Biomass size reduction

Various mechanical size reduction methods are employed to increase the digestibility of lignocellulosic biomass such as chipping, shredding, grinding, coarse size reduction and milling (Laser et al., 2002). These pretreatment methods decrease the cellulose crystallinity and the degree of polymerization as well as increase the specific surface area (Sanchez and Cardona, 2008). Menegol et al. (2016) also revealed that physical pretreatment leads to higher ethanol production after delignification of elephant grass. However, studies demonstrated that more reduction of biomass particles i.e. smaller than 0.4 mm has no significant effect on yield and rate of hydrolysis (Chang et al., 1997). The energy demand for mechanical comminution of lignocellulosic material depends on agricultural biomass features and final particle size (Cadoche and López, 1989). Higher energy demand for milling procedure is the main drawback of this technique (Hideno et al., 2009). Studies suggest that milling before pretreatment have several benefits like low consumption of milling energy and no production of fermentation inhibitors. It also reduces the cost of separating solids from liquids by decreasing the solids to liquids ratio (Zhu et al., 2010). Kim et al. (2013) compared three different milling method such as planetary, attrition and ball milling. Ball milling was less effective in reducing the size of biomass as compared to attrition milling and planetary milling. The highest amount of galactose and glucose were produced by planetary mill method rather than other tested milling methods. The point to be noted is that all the mill pretreatment methods do not produce any toxic compounds e.g. levulinic acid and hydroxymethyl furfuraldehyde (HMF). It makes mill pretreatment a good choice of initial pretreatment for a broad range of lignocellulosic feedstocks. Application of wet disk milling and ball milling used to estimate the effectiveness of milling on sugarcane bagasse. According to assessment, hydrolysis yield of xylose and glucose under optimum condition of mill treated bagasse were 72.1% and 78.7% respectively. Whereas maximum xylose and glucose yielded for bagasse wet milling-treated were 36.7% and 49.3% respectively (da Silva et al., 2010; Hideno et al., 2009).

Extrusion

Extrusion is a developed method of mechanical comminution in which the access of enzyme is widened to strike well-exposed carbohydrates (Zhan et al., 2006). It includes rapid mixing, less residence period, high shear, moderate barrel temperature, no furfural, no washing, and conditioning. Moreover, most possibilities of continuous operation are considered among the benefits of this method (Karunanithy et al., 2008; Karunanithy and Muthukumarappan, 2011). Various factors should be handled such as compression ratio, temperature, and speed of screw to obtain the extrusion pretreatment efficiency (Karunanithy and Muthukumarappan, 2010). In another experiment, Yoo et al. (2011) obtained 94.8% glucose conversion after enzymatic hydrolysis (glucose yield of 0.37 g/g biomass). Lee et al. revealed that Douglas fir was extruded before hydrolysis and it showed 62.4% conversion of the feedstock into glucose. They reported its ability to run continuously with zero effluent waste. Extrusion pretreatment method is feasible to apply on an industrial level and also don’t cause an environmental problem (Lee et al., 2009a).

Microwave

Microwave irradiation is broadly used for the pretreatment of lignocellulosic feedstock because of numerous reasons such as lower energy demand, less production of inhibitors, easy operation, degrades structural organization of cellulose fraction and high heating capacity in short duration (Hu and Wen, 2008). In microwave irradiation process electromagnetic field is employed. For the bioethanol production, this approach is applied for the pretreated biomass structural disruption. Microwave attacks the polar bond by vibrating the structure until material inside becomes heated. As a result, complex lignocellulosic structure fractures and enlarge the surface area for the subsequent enzymatic attack. Microwave treatment is reckoned as an improvement effort through assisting other treatment methods. Recently, the microwave was used to assist hydrothermal hydrolysis of sago pith waste (Ma et al., 2009). The microwave assisted hydrothermal hydrolysis consumed only 33 kJ and 69 kJ per every gram production of glucose and ethanol respectively, which graded as energy efficient. Moreover, for more actual breakdown the mild alkali reagents addition is preferred. Additionally, it has been revealed microwave based alkali pretreatment of switchgrass produced approximately 70-90% sugars (Hu and Wen, 2008).

Zhu et al. (2015a, 2015b, 2016) checked the effects of microwave on chemically pretreated *Miscanthus*. As compared to conventional heating, sulfuric acid and sodium hydroxide pretreatment generated 12 times higher yield in half of the time consumed for heating. Primarily, this was due to lignin solubilization and pre-disruption of crystalline cellulose with the chemical pretreatment. When pretreated with 0.2 M sulfuric acid at 180 °C temperature for 20 minutes, the maximum glucose yield obtained was 46.7%, and sugar yield was 75.3% (Zhu et al., 2015a, 2015b). Likewise, Zhu et al. (2016) established an orthogonal design to improve the microwave pretreatment of wheat straw and also enhance the ethanol production from 2.678-14.8%.

Physio-chemical pretreatment

Steam explosion

Previously, it was known as steam explosion; steam pretreatment is a physicochemical strategy commonly used for lignocellulose biomass hydrolysis (Agbor et al., 2011). This method exposes the biomass at high-pressure steam for a few seconds initially at the range 160 °C to 260 °C (Sun and Cheng, 2002). The hydrolysis of hemicellulose into glucose and xylose monomers is carried out by the acetic acid formed from the hemicellulose acetyl groups during this pretreatment. Hence this procedure is also known as auto-hydrolysis (Mosier et al., 2005). Several factors such as resistance time, the size of biomass, moisture content and temperature affect the pretreatment (Rabemanolontsoa and Saka, 2016). The presence of H_2SO_4, CO_2 or SO_2 as a catalyst can enhance the actual efficiency of this process. Without these catalysts, the acidic catalyst has been found most effective for minimized the production of inhibitor compounds, recovery of hemicellulose sugar and better enzymatic hydrolysis. This pretreatment has been found effective for agricultural residue and hardwoods pretreatment. Steam pretreatment has some advantages such as low energy requirements, limited chemicals use, no recycling cost and environment-friendly. On the other side, the risk of high-temperature formation of fermentation inhibitory compounds, lignin-carbohydrate matrix incomplete digestion and the need to wash the hydrolysate (Agbor et al., 2011). After 72 hours of enzymatic hydrolysis, corn stover pretreated with steam pretreatment under catalyst (SO_2) has been shown to give high yields of sugar such as almost 80% overall xylose yield and nearly 90% overall glucose yield (Öhgren et al., 2005). Ethanol can be produced from lignocellulosic biomass employing steam pretreatment followed by fermentation and enzymatic hydrolysis. Sugar yield of both cellulose and hemicellulose are critical parameters for an economically reasonable for ethanol production process (Öhgren et al., 2007).

Liquid hot water

Liquid hot water, also known as hot compressed water is same like stream pretreatment method. However, as its name indicates, water is used at high pressure up to 5 Mpa and high temperature 170–230 °C instead of steam. This is also variously mentioned as hydro thermolysis, aquasolv, hydrothermal pretreatment and aqueous fractionation. It removes lignin offering extra accessible cellulose and hemicellulose (Agbor et al., 2011; Laser et al., 2002; Yang and Wyman, 2004). Liquid hot water is an effective method to treat different biomass types including softwoods (Rabemanolontsoa and Saka, 2016). Water-insoluble material, solids enriched with cellulose and liquid fraction such as water, inhibitors, solubilized hemicellulose are generated as slurry through the pretreatment procedure. In liquid hot water control pH between 4–7 is appropriate to avoid the sugar degradation and inhibitors formation.

Laser et al. (2002) achieved maximum solubilized hemicellulose with minimum inhibitors production and pH control during hot water pretreatment of corn stover at 190^{o}C for 15 minutes. They obtained conversion of cellulose to glucose at the rate of 90% through the enzymatic hydrolysis. This pretreatment method is economically and environmentally attractive because chemical catalyst or acid is not used in this process (Mosier et al., 2005). Its advantages include low-temperature requirement, no inhibitory compounds formation at high temperature, and low-priced solvent of liquid hot water process (Agbor et al., 2011; Yang and Wyman, 2004).

Ammonia fiber explosion

Soaking aqueous ammonia, ammonia fiber explosion and ammonia recycle percolation are the methods employed for the lignocellulosic biomass pretreatment in which liquid ammonia is used (Agbor et al., 2011). In soaking ammonia, biomass is treated with aqueous ammonia in a batch reactor at temperature (30–60 °C) which decrease the through putting during the process of pretreatment (Kim and Lee, 2005a). Ammonia fiber explosion pretreatment is similar to a steam explosion, which treats lignocellulosic biomass with ammonia on specific temperature (60–100 °C) and high pressure (250–300 psi) for a short period. The operational parameters involved in the ammonia fibers explosion are temperature, blowdown pressure, water loading, and ammonia loading (Holtzapple et al., 1991). It causes the swelling and phase change of biomass cellulose crystallinity leading to increasing the reactivity of leftover carbohydrates after pretreatment. As compared to other pretreatment methods, ammonia fiber explosion does not produce inhibitors which are extremely desirable for downstream processing. The lack of extra steps such as detoxification, water washing, reuse of large quantity of water and recovery make the overall cost significantly low. If ammonia fiber explosion pretreatment is employed under optimized condition more than 90% hemicellulose and cellulose can be converted into fermentable sugar (Uppugundla et al., 2014). Ammonia recycle percolation is a powerful method as compared to any other conventional pretreatment methods to remove lignin and without any contamination e.g. sulfur and sodium (Yoon et al., 1995).

Ammonia recycle percolation process does not affect the cellulose but makes hemicellulose soluble. This method needs high amount of energy to maintain temperature. Ammonia fiber explosion and ammonia recycle percolation more efficient for agriculture residues and herbaceous plant (Alvira et al., 2010; Kim and Lee, 2005b). Belkacemi et al. (1998) produced ethanol from agriculture residue and forages through the pretreatment of ammonia fiber explosion. They pretreated the forage-based lignocellulosic biomass such as barley straw, corn stalk, alfalfa, reed canarygrass and timothy grass and obtained 60-70% sugar yield by using ammonia fiber explosion pretreatment. There are several advantages include ammonia recovery, no inhibitors production, lignin redistribution and ability to accomplish theoretical yield level (Sun and Cheng, 2002). This pretreatment has major challenge of total energy consumption cost (Banerjee et al., 2009).

Carbon dioxide (CO_2)

For bioethanol production, the use of carbon dioxide (CO_2) as supercritical liquid technology is a feasible strategy. It provides the modification of possible pretreatment process and usually used for coffee decaffeination technique (Zheng et al., 1998). Supercritical CO_2 pretreat the lignocellulose biomass which means that the gas behaves like a solvent. At high temperature, supercritical carbon dioxide passes through a vessel having biomass. The vessel temperature is kept high for several minutes. At high-temperature CO_2 enter the biomass and forms carbonic acid which causes hemicellulose hydrolysis. High-pressure gas disorders the biomass structure and increase the accessible surface area (Hendriks and Zeeman, 2009; Kim and Hong, 2001; Zheng et al., 1995). Biomass without sufficient moisture is not suitable for this pretreatment process (Kim and Hong, 2001). However, supercritical liquid technology is considered beneficial because it contains both features liquid insolvent and gas transfer in mass. As compared to steam ammonia and steam explosion, this process is favorable for the production of ethanol,because it produces low inhibitory products and removes lignin at more feasible way (non-acidic and non-corrosive). Moreover, CO_2 as the supercritical fluid pierce the crystalline easy and also not degrade the required sugar monomers because of its mild environment (Zheng et al., 1998).

Wet oxidation

In wet oxidation pretreatment method, biomass is subjected to high temperature i.e. 170–200 °C and high pressure i.e. 500–2000 kPa for 10–15 minutes. Wet oxidation is a simple and easy method. This had earlier been employed for soil remediation and wastewater treatment. This approach degrades the lignocellulosic material and produces fewer inhibitors, eliminates lignin as well as lower cellulose. Hence it provides a suitable condition for the procedures like fermentation and enzymatic hydrolysis to work on the pretreated product. However, common challenges like energy efficiency and capital cost are associated with this method (Banerjee et al., 2009; Chaturvedi and Verma, 2013; Martín et al., 2008). Wet oxidation method is suitable for the lignin enriched biomass residue. The efficiency of this approach depends upon three factors i.e. temperature, reaction time and oxygen pressure. In this process, water behaves like an acid and catalyzes hydrolytic reactions when the temperature is above 170 °C. Small pentose monomers are formed after breaking down of hemicellulose. The lignin undergoes oxidation, while the cellulose is least affected by wet oxidation pretreatment. Besides these, in wet oxidation additional chemical agents such as sodium carbonate and alkaline peroxide decrease the reaction temperature and improved hemicellulose degradation along with decreased production of inhibitors e.g. furfurals and furfurl aldehydes (Banerjee et al., 2011).

Banerjee et al. (2009) have maximized the wet oxidation condition for the production of ethanol from rice husk. Reducing sugar yields higher than 70% was recorded after this pretreatment method. Rice husk pretreated with Alkaline Peroxide Assisted Wet Air indicated result solubilization of 88 and 67% lignin and hemicellulose, respectively. The glucose amount improved 13 folds as compared to rice husk without treatment.

Chemical pretreatment

Dilute acid pretreatment

Diluted acid pretreatment is a conventional method and forms inhibitory products. However, it is commonly used for bioethanol production from lignocellulosic feedstock on industrial scale (Saha et al., 2005a; Sassner et al., 2008; Sun and Cheng, 2005). Based on the type of end application, two kinds of acid pretreatment are established;

temperature less than 120 °C for long duration 30 to 90 minutes and high temperature more than 180 °C for 1 to 5 minutes respectively. Various kinds of reactors are also employed such as plug flow, shrinking-bed, percolation and flow-through. However, before further processing, inhibitors generated in acid pretreatment should be removed. To make the process economically feasible, the concentrated acid should be recovered after hydrolysis (Digman et al., 2010; Sassner et al., 2008). For the pretreatment of lignocellulosic biomass, different acids have been applied on industrial scale such as phosphoric acid, hydrochloric acid, nitric acid, and dilute sulphuric acid. Various organic acids such as acetic acid, lactic acid, maleic acid and peracetic acid are being used in the acid pretreatment of lignocellulosic biomass (Balat et al., 2008; Digman et al., 2010; Refaat, 2012). In acid pretreatment, rye straw and bermudagrass were pretreated with 1.5% sulphuric acid resulted in production of 22.93% reducing sugars, while hydrolysis yielded 19.71 reducing sugars respectively (Sun and Cheng, 2005). Another study revealed 204.1 mg/g of reducing sugars from Bermuda grass pretreated with 1.2 % dilute sulfuric acid for 1 hour at 121 °C (Sun and Cheng, 2005). In another study, bioethanol was produced through dilute acid pretreatment and silver grass using as feedstock (Guo et al., 2008). The silver grass produced 64.3% ethanol and 70–75% xylan sugars after diluted acid pretreatment at 121 °C for 30 minutes (Aditiya et al., 2015). Di-carboxylic acid: Oxalic acid, maleic acids and other kinds of are known as dicarboxylic acids are being utilized by the researchers in order to overcome the disadvantages of sulfuric acid. Dicarboxylic organic acid show high pKa values, which make this type of acids more effective for carrying out the hydrolysis of substrate over variety of pH and temperature (Lee and Jeffries, 2011)**.** Lee and coworkers (2011) pretreated the corn cobs with oxalic acid and heated for 26 minutes at 168 °C temperature. A total 13% sugar yield was found by the oxalic acid pretreatment (Lee and Jeffries, 2011). Maleic acid is another dicarboxylic acid which is commonly employed for the acid pretreatment. (Mosier et al., 2002). Lee and Jeffries (2011) examined the effect of sulfuric, maleic and oxalic acid on lignocellulosic biomass degradation and hydrolysis at same combined severity factor (CSF) during hydrolysis. Glucose and xylose concentration was found to be highest in maleic acid as compared to oxalic and sulfuric acid at low combined severity factor (CSF). When the maleic acid was employed for the pretreatment of biomass, the subsequent fermentation with biomass which was pretreated yielded maximum ethanol (19.2 g/L) at CSF 1.9 (Lee and Jeffries, 2011).

Pretreatment of lignocellulosic biomass with sulfuric acid is a conventional method because of its low cost. Hence, it has certain disadvantages such as corrosion of reaction vessel and production of inhibitory compounds (Lee and Jeffries, 2011). The toxic and corrosive nature of various acid needs appropriate material for constructing the reactor which can sustain the corrosive nature of acid and experimental conditions (Saha et al., 2005a). Whereas, dilute acid pretreatment acid does not need acid recovery with the insignificant acid loss (Refaat, 2012). Less amount of inhibitors compounds are produced by the Oxalic acid (Lee and Jeffries, 2011). The advantages discussed above, the maleic acid in specific has khyd/kdeg which helps cellulose hydrolysis to glucose and also over glucose degradation (Mosier et al., 2002).

Mid alkali pretreatment

As compared to acid treatment, alkali pretreatment methods commonly employed at ambient pressure and temperature. This breaks down extra lignin content and converts into a better available condition for hydrolysis afterward (Kumar and Wyman, 2009; Refaat, 2012). Alkali reagents are used that are hydroxyl derivatives of sodium, calcium, potassium and ammonium salts. Sodium hydroxide was found to be effective as compared to these hydroxyl derivatives (Kumar and Wyman, 2009). However, with the alkali pretreatment, the solubility of hemicellulose and cellulose is little as compared to acid pretreatment. Disrupted lignin structure, decreased the degree of polymerization and high internal cellulose surface area improves the solubility (Taherzadeh and Karimi, 2008).

Sun et al. (1995) improved the temperature and pretreatment utilizing 1.5% sodium hydroxide released 80% hemicellulose and 60 % lignin at 20 °C for 144 hours. Zhao et al. (2008) used different biomass such as switchgrass, softwoods, wheat straw and hardwoods to check the effect of sodium hydroxide containing less than 26% lignin. However, no effect on softwood of dilute sodium hydroxide was observed with lignin content larger than 26% (Kumar and Wyman, 2009).

As compared to other pretreatments, e.g. Acid pretreatment, mild alkali pretreatment is less harsh and can also be effectively carried out at ambient condition. However, higher temperature is required if the pretreatment is needed to be conducted for an extended time. Further to remove the inhibitors like lignin, a neutralizing step is necessary (Brodeur et al., 2011). Lime pretreatment is cheap as compared to the alkaline agents (Brodeur et al., 2011). Park et al., (2010 a,b) adjusted the lime pretreatment method through neutralizing lime with carbon dioxide before hydrolysis and removed the solid-liquid separation step resulting in 89% glucose recovery from leaf star rice straw. They also applied the alteration to study the fermentation (SSF) and simultaneous scarification by using *Pichia stipites* and *Saccharomyces cerevisae*. After 79 hours fermentation at 30 °C found 74% increase in ethanol yield.

Organosolv pretreatment

Organosolv is applied to dissolve lignin from lignocellulose biomass (Zhao et al., 2009). This method is also considered as one of chemical pretreatment (Zhao et al., 2009), that includes the application of organic solvents e.g. acetone, ethanol, ethylene glycol, methanol, and tetrahydro furfuryl alcohol (Mesa et al., 2011) Usually, acid, salt or base are the catalysts of this process (Bajpai, 2016). Organic or inorganic acids (sulfuric acid and hydrochloric acids) and bases (lime, sodium hydroxide, ammonia) are used as catalysts (Zhao et al., 2009). Lignin is a value-added product which is separated from biomass by this process that reveals enzymatic hydrolysis of cellulose fiber which leads to higher conversion of biomass. Apart from lignin, during organosolv pretreatment hemicellulose syrup C5 and C6 and cellulose fraction is also produced (Agbor et al., 2011). A study by Li et al. (Li et al., 2009) applied phosphoric acid and acetone and reported 93% quality bioethanol production from lignocellulosic biomass by using the organosolv method. High-quality bioethanol is the main advantage of this approach (Zhao et al., 2009). The disadvantages are the low-boiling point of organic solvents, high risk of high-pressure operation, high risk of volatility of harsh solvents (Agbor et al., 2011; Sun and Chen, 2008). A high flame of harsh solvents and large fire explosions can damage without the lack of particular safety measures. A method that treats the biomass at high temperature 100 °C and pressures 1 atm with the mixture of phenol, water, and HCl is termed, Battelle is the type of Organosolv (Villaverde et al., 2010). The Organosolv pretreatment process is shown in (*Fig. 6*)

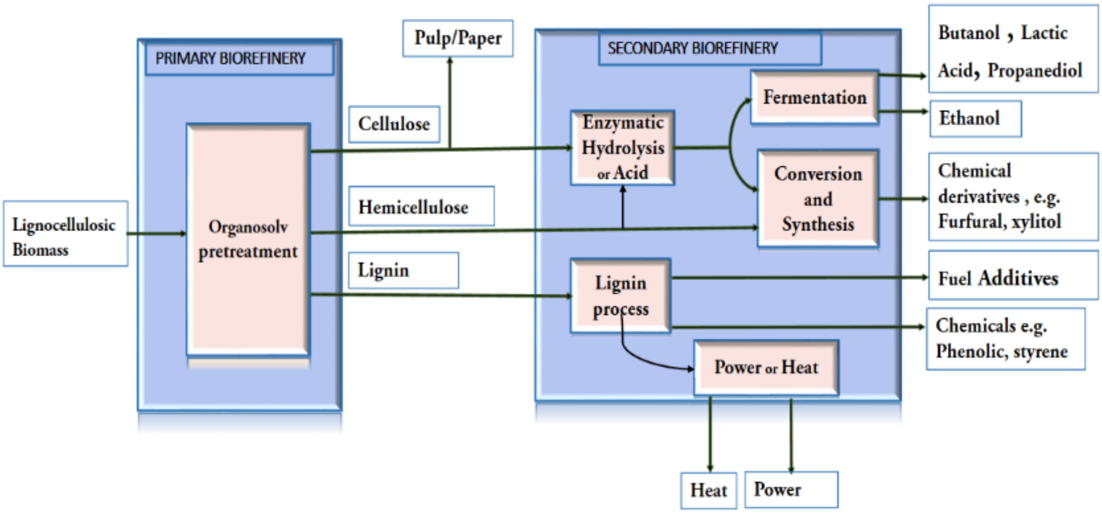

Figure 6. *Organosolv pretreatment process (Sidiras and Salapa, 2015; Zhang et al., 2016)*

Ozonolysis

In Ozonolysis pretreatment ozone gas used as an oxidant to break up lignin, hemicellulose and enhance the biodegradation of cellulose (Balat, 2011). It has been used to eliminate the lignin in a different kind of biomass e.g. poplar sawdust (Vidal and Molinier, 1988), green hay, bagasse, peanut and pine (Neely, 1984). After the removal of 60% lignin, cellulose enzymolysis rate can rise fivefold by the pretreatment. The lignin content can also be decreased from 29% to 8%, and the quality of the enzymatic hydrolysis yield can be increased by 57% (Sun and Cheng, 2002). Ozonolysis can also eradicate the lignin efficiently at normal pressure and room temperature similar to another chemical pretreatment method. This pretreatment method has several advantages. It is environmentally friendly because toxic inhibitors are not produced and have no effect on post-pretreatment processes e.g. yeast fermentation and enzymatic hydrolysis (Quesada et al., 1999; Sun and Cheng, 2002). Lack of degradation by-products which leads to less complication in the subsequent hydrolysis steps is considered most beneficial (García-Cubero et al., 2009). On the other hand, an enormous amount of expensive ozone is used to treat lignocellulosic material which is the main disadvantage (Sun and Cheng, 2002).

Ionic liquid pretreatment

Ionic liquid pretreatment is considered as a green and sustainable method using ionic liquid fractures. Due to this, covalent structure between hemicellulose, lignin and cellulose are disrupted due to the strong hydrogen bond acceptors of the ionic liquid (Refaat, 2012; Swatloski et al., 2002). It is reported that the most effective ionic liquids are 1-allyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride (Vitz et al., 2009). As compared to dilute acid pretreatment, ionic liquid pretreatment yields less crystallinity, the large surface area of cellulose and less lignin obtained as well as an additional increase in enzymatic hydrolysis. (Li et al., 2010). Ionic liquid pretreatment advantages include zero vapor pressure, large stable temperature range and appropriate chemical stability (Ouellet et al., 2011). It has some of the disadvantages such as low-cost recovery technology, toxicity to microorganisms and enzymes. This process should be considered to recover lignin and hemicellulose from solutions after extraction of cellulose (Hayes, 2009; Lee et al., 2009b). The ionic pretreatment process is mention in diagram (*Fig. 7*) (Brandt et al., 2013).

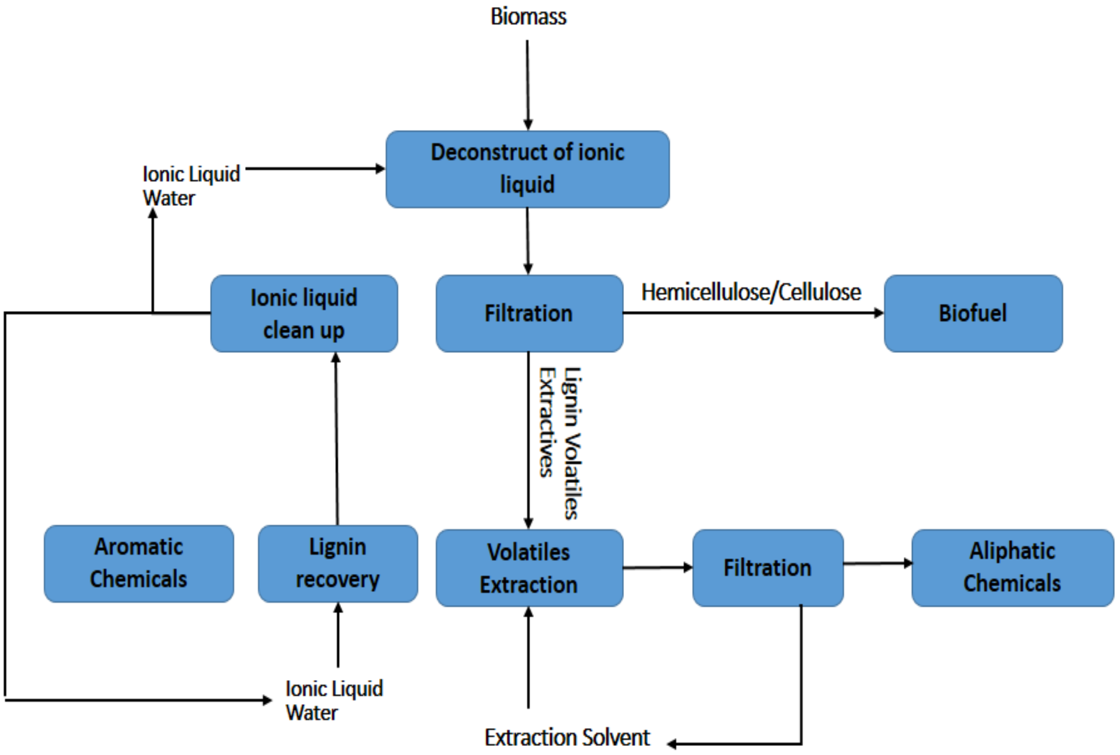

Figure 7. *Ionic Pretreatment Procedure (Brandt et al., 2013)*

Biological pretreatment

For the degradation of lignocellulose biomass, natural microorganisms possessing enzymes (bacteria, brown-white and soft rot fungi) are employed that are capable cell wall deconstruction (Talebnia et al., 2010). Biological pretreatment method does not produce any unwanted products as compared to chemical and physical pretreatment. Additionally, high pressure, acids, alkali, high temperature or any reactive species are not compulsory for this pretreatment (Zhang et al., 2011). White- and soft-rot fungi contain lignin-degrading enzymes like lignin peroxidases, manganese-dependent peroxidases, polyphenol oxidases, and laccases which are effective for the lignin degradation. Degradation by microorganisms, mode of action and features depends on targeted biomass component. For example, white and soft-rot fungi are considered most useful for degradation of lignin by using their lignin-degrading enzymes, and brown-rot fungi mainly attack cellulose (Sánchez, 2009; Sun and Cheng, 2002).

Wheat straw pretreated with low cellulose degrading fungus and high lignin degrading fungus resulted in a reduction in the concentration of inhibitors and acid loading for hydrolysis as well as increase the fermentable sugar. Ethanol yield and volumetric productivity with *Pichia stipitis* were 0.48 g/ g and 0.54 g/L h respectively (Kuhar et al., 2008). Biological pretreatment is efficient in comparison with any others pretreatment methods because it does not require chemicals. Furthermore, low energy and mild environmental condition are also considered as an advantage. However, the main drawback to develop biological methods is low hydrolysis rate obtained in biological materials (Sun and Cheng, 2002) (Salvachúa et al., 2011).Most lignin degrading microorganisms also degrade not only lignin but also cellulose and hemicellulose (Eggeman and Elander, 2005). Extensive research is required for the implementation of these microorganisms on a large commercial scale for biological pretreatment of lignocellulose biomass.

Conclusions

Various pretreatment methods have been developed for the delignification of lignocellulose biomass to obtain ethanol. However, we have concluded through the critical analysis, the correct choice of pretreatment should depend on the lignocellulosic biomass properties and features. Besides, a single pretreatment technique does not exist currently, which is economically practicable and environmentally friendly manner for the complete biomass delignification. Still, combined pretreatment techniques have found successful in the ethanol production, however, to achieve the total potential of the combined pretreatment method, much research required to be performed.

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