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Review

Augmented digestion of lignocellulose by steam explosion, acid and alkaline pretreatment methods: A review

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ABSTRACT

Lignocellulosic materials can be explored as one of the sustainable substrates for bioethanol production through microbial intervention as they are abundant, cheap and renewable. But at the same time, their recalcitrant structure makes the conversion process more cumbersome owing to their chemical composition which adversely affects the efficiency of bioethanol production. Therefore, the technical approaches to overcome recalcitrance of biomass feedstock has been developed to remove the barriers with the help of pretreatment methods which make cellulose more accessible to the hydrolytic enzymes, secreted by the microorganisms, for its conversion to glucose. Pretreatment of lignocellulosic biomass in cost effective manner is a major challenge to bioethanol technology research and development. Hence, in this review, we have discussed various aspects of three commonly used pretreatment methods, viz., steam explosion, acid and alkaline, applied on various lignocellulosic biomasses to augment their digestibility alongwith the challenges associated with their processing.

Contents

1. Introduction

Over the last few decades, the security issues related to fast depleting oil reserves and rising energy consumption are of prime concern globally owing to over-exploitation of fossil fuels. These security concerns have a negative impact not only on the economy but also on the environment raising issues such as global warming and air pollution. As the economy of most of the countries depends on oil, the consequences of inadequate oil availability could be severe. Now-a-days, bioethanol has been recognized as a promising future alternative to petroleum-derived transportation fuels (Dias, Junqueira, Rossell, Filho, & Bonomi, 2013) owing to its high octane number (Hu, Heitmann, & Rojas, 2008), low cetane number and high heat of vaporization (Jin, Fang, Zhang, Zhou, & Zhao, 2012) as it is envisaged to be appropriate for mixing with petrol. Hence, production of ethanol from lignocellulosic biomasses has attracted many researchers due to their availability, abundance and relatively low cost (Ferreira, Gil, Queiroz, Duarte, & Domingues, 2010; Njoku, Ahring, & Uellendahl, 2012; Singhania, Patel, Sukumaran, Larroche, & Pandey, 2013). It is worth mentioning here that the major constituents of the lignocellulosic biomass, used for bioconversion, are cellulose, hemicellulose and lignin polymers (Ruffell, Levie, Helle, & Duff, 2010) which are closely associated with each other to constitute the

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cellular complex of the vegetal biomass making it extremely resistant to microbial attack (Sousa, Chundawat, Balan, & Dale, 2009; Park et al., 2010; Weerachanchai, Leong, Chang, Ching, & Lee, 2012).

The bioconversion of lignocellulosic biomass to ethanol involves three major unit operations: pretreatment, enzymatic hydrolysis and fermentation (Ruiz et al., 2012). The overall objective of any pretreatment method is to remove lignin (Govumoni, Koti, Kothagouni, Venkateshwar, & Linga, 2013) and hemicellulose (Mosier et al., 2005) in order to reduce the crystallinity as well as the degree of polymerization of cellulose and increase the porosity of the lignocellulosic materials (Joshi et al., 2011). This makes the cellulose susceptible to enzymatic hydrolysis (Kaparaju & Felby, 2010; Liew, Shi, & Li, 2011; Xiao, Yin, Xia, & Ma, 2012) to yield sugars. Further, it is essential that any effective pretreatment method must be conducive to improve the formation of sugars by hydrolysis (Zhou, Zang, Gong, Wang, & Ma, 2012; Taherzadeh & Karimi, 2008; Lamsal, Yoo, Brijwani, & Alavi, 2010; Radeva, Valchev, Petrin, Valcheva, & Tsekova, 2012), to limit or prevent the degradation or loss of carbohydrates, to avoid the formation of degradation products that are inhibitory to the subsequent hydrolysis and fermentation processes (Talebnia, Karakashev, & Angelidaki, 2010; Thulluri, Goluguri, Konakalla, Shetty, & Addepally, 2013) and minimizing energy input for cost effectiveness (Arslan & Eken-Saracoglu, 2010). Pretreatment results must also be weighed against their impact on the ease of operation, cost of the downstream processes and the trade-off between several costs including operational, capital and biomass costs (Wyman, 1999; Zhu & Pan, 2010).

Hence, cost effective pretreatment of lignocellulosic biomass is a major challenge of cellulose-bioethanol technology (Krishnan et al., 2010). However, there is a huge scope in lowering the cost of pretreatment process through extensive research and development for which several pretreatment techniques like physical (milling and grinding), physico-chemical (steam explosion/autohydrolysis, hydrothermolysis and wet oxidation), chemical (alkali, dilute acid, oxidizing agents and organic solvents) and biological processes have been used for efficient conversion of the structural carbohydrates to fermentable sugars (Balat, 2011). This report evaluates the suitability of most commonly employed approaches, viz., steam explosion, acid and alkaline pretreatments, for augmenting the digestibility of complex lignocellulosic biomasses into fermentable sugars on the basis of relevant studies investigated regarding these pretreatment methods.

2. Steam explosion pretreatment

Steam explosion, also known as autohydrolysis, is the most widely employed physico-chemical pretreatment method for any lignocellulosic biomass (Chandra, Bura, & Mabee, 2007; Balat, 2011; Wanderleya, Martín, Rocha, & Gouveia, 2013) because of its potential for disrupting crystallinity of cellulose, delignification (Duff & Murray, 1996; Balat, Balat, & Cahide, 2007) and easy hydrolysis of the hemicelluloses (Lee, Jameel, & Venditti, 2010). It acts as an excellent environment-friendly method as it replaces chemical reagents (Egues, Sanchez, Mondragon, & Labidi, 2012) and enhances the enzymatic hydrolysis of cellulosic biomass (Zhang et al., 2011; Shamsudin et al., 2012). This is one of the biomass fractionation processes which include steam explosion, aqueous separation and hot-water systems.

The technology of steam explosion pretreatment has been investigated for ethanol production from a wide range of feedstocks, viz., wheat straw (Ballesteros et al., 2006), sunflower stalks (Vaithanomsat, Chuichulcherm, & Apiwatanapiwat, 2009), *Pinus patula* (Chacha, Toven, Mtui, Katima, & Mrema, 2011), rice straw (Chen, Pen, Yu, & Hwang, 2011), switchgrass and sugarcane bagasse (Ewanick & Bura, 2011), corn stover (Yu, Feng, Xu, Liu, & Li, 2011) and *Eucalyptus globulus* (Martin-Sampedro et al., 2012). Albeit, steam explosion is found to be the most cost effective option for hardwood and agricultural residues or herbaceous biomass but less effective for softwood due to its low content of acetyl groups in the hemicellulose portion (Prasad, Singh, Jain, & Joshi, 2007).

In steam explosion, the biomass is rapidly heated by high-pressure saturated steam for a set period of time and then the pressure is swiftly released (Kumar & Murthy, 2011) causing the steam to expand within the lignocellulosic matrix which results in the separation of individual fibers disrupting the cell wall structure (Mabee et al., 2006; Horn & Eijsink, 2010; Boluda-Aguilar, Garcia-Vidal, Gonzalez-Castaneda, & Lopez-Gomez, 2010; Martin-Sampedro, Martin, Eugenio, Revilla, & Villar, 2011). The action mode of steam explosion is found to be similar to that of acid-based chemical pretreatment except that during steam explosion, more concentrated sugars are obtained because the biomass is heated rapidly by steam and much less moisture exists in the reactor (Jorgensen, Kristensen, & Felby, 2007). During this pretreatment mode, the hemicelluloses of the lignocellulosics are often hydrolyzed by organic acids (Jacquet et al., 2011) such as acetic acids and other acids which are formed from acetyl or other functional groups released from biomass (Weil et al., 1997). Acetic acid hydrolyzes xylan polymers into xylose and xylose oligomers (Vaithanomsat et al., 2009). Further degradation of sugars might also happen during steam explosion due to acidic conditions. To minimize this further degradation during steam pretreatment, the biomass must be separated from the condensate (Allen, Schulman, Lichwa, & Antal, 2001) either by keeping the pH between 5 and 7 by the addition of an external alkali (Weil et al., 1998; Li, Henriksson, & Gellerstedt, 2005) or by applying a two-step steam pretreatment (Chen et al., 2011). It is however not clear whether the higher ethanol yield outweighs the additional costs of a second pretreatment step (Shahbazi, Li, & Mims, 2005) but it definitely offers some additional advantages such as higher bioethanol yields, better use of raw material and lower enzyme dosages required for enzymatic hydrolysis (Tomas-Pejo, Oliva, & Ballesteros, 2008).

The major physico-chemical changes of lignocellulosic biomass during the steam explosion pretreatment are attributed to the hemicellulose removal and lignin transformation which help to improve the digestibility of biomass to enzymes (Kabel, Bos, Zeevalking, Voragen, & Schols, 2007). This pretreatment causes the breakdown of biomass components by steam heating and shearing forces due to the expansion of moisture and hydrolysis of glycosidic bonds by the organic acid formed during the process (Avellar & Glasser, 1998; Jacquet, Vanderghem, Blecker, & Paquot, 2010). It also induces the melting of lignin and its partial depolymerisation through the homolytic cleavage of the predominant β-*O*-4 ether and other acid-labile linkages producing a series of cinnamyl alcohols derivatives (Tanshashi, 1990) and condensation byproducts (Ramos, 2003). There have been some evidences indicating that these products are strong inhibitors to microbial growth (Excoffier & Vignon, 1991) and that detoxification strategies are required to increase the fermentability of lignocellulosic hydrolysates to fuels and chemicals (Larsson et al., 1999).

The factors that affect steam explosion pretreatment are residence time, temperature, chip size and moisture content (Negro, Manzanares, & Oliva, 2003; Talebnia et al., 2010). Optimal hemicellulose solubilization and hydrolysis could be achieved either by high temperature and short residence time (270 °C, 1 min) or lower temperature and longer residence time (190 °C, 10 min) (Duff & Murray, 1996). Though the steam explosion processes occur in temperature ranges from 200 °C to 280 °C with retention time varying from 2 to 10 min but under these conditions, thermal degradation of cellulose into sugars takes place (Quievy et al., 2009; Jacquet et al., 2011). Ruiz, Cara, Manzanares, Ballesteros, and Castro (2008) and Horn, Nguyen, Westereng, Nilsen, and Eijsink (2011) have also

reported similar results when they found highest glucose yield from sunflower stalks and wheat straw after steam pretreatment at the respective temperature range of 220 °C and 210 °C. However, lower temperature and longer residence time were found to be more favourable (Wright, 1998) because hemicelluloses were lost and inhibitors, particularly 5-HMF (Hydroxymethyl Furfural), were generated in the process at higher pretreatment severities (Martin-Sampedro et al., 2012). Besides temperature and residence time, smaller particle size of the lignocellulosic biomass also facilitated the process of heat transfer during steam explosion (Brownell & Saddler, 1984; Ballesteros, Oliva, Negro, Manzanares, & Ballesteros, 2002). The steam requirement for pretreating aspen chips increased with increase in chips size and moisture content (Brownell, Yu, & Saddler, 1986) and the steam explosion was stated to be desirable only when hardwood chips with low moisture content were used (Ramos, Breuil, Kushner, & Saddler, 1992). Likewise, DeLong (1983) also claimed that explosion was an essential step towards the production of highly accessible substrates for enzymatic hydrolysis.

In some cases, addition of some gaseous/liquid acidic chemicals, primarily SO_2, H_2SO_4 and CO_2 etc. were used as catalysts to impregnate the biomass prior to steam explosion (Fein et al., 1991; Ropare, Marchal, Pourquie, & Vandecasteele, 1992; Boussaid, Robinson, Cai, Gregg, & Saddler, 1999; De Bari, Nanna, & Braccio, 2007; Ferreira-Leitao et al., 2010; Chen et al., 2011) because the addition of catalyst in steam explosion could not only decrease time and temperature to improve enzymatic hydrolysis but also the production of inhibitory compounds and led to more complete removal of hemicelluloses (Stenberg, Tengborg, Galbe, & Zacchi, 1998). The highest recovery of glucose and xylose was obtained after steam pretreatment of H_2SO_4 impregnated wheat straw at 190 °C for 10 min (Ballestros et al., 2006; Linde, Jakobsson, Galbe, & Zacchi, 2007). Likewise, Chacha et al. (2011) found that on a given cellulose content, the yield of reducing sugars increased from 29% under the mildest steam pretreatment conditions (180 °C, 1.5% SO_2) to 91% under the most severe steam pretreatment conditions (225 °C, 3% SO_2). The studies of Chacha et al. (2011) also confirmed that SO_2 was more appealing than H_2SO_4 in steam explosion since the former required milder and much less expensive reactor material, generated less gypsum, yielded more xylose, and produced more digestible substrate with high fermentability. At the same time, SO_2-impregnated steam explosion was also considered the only known pretreatment technique that could effectively make softwoods more digestible (Hahn-Hagerdal, Galbe, Gorwa-Grauslund, Liden, & Zacchi, 2006; Zheng, Pan, & Zhang, 2009) by improving their hydrolyzability (Bura, Chandra, & Saddler, 2009). However, encouraging results were obtained by Ferreira-Leitao et al. (2010) when they compared the steam pretreatment performance with CO_2 and SO_2 because some characteristics of CO_2, namely, high availability, low cost, low toxicity, low corrosivity and low occupational risk, were very attractive.

Although the steam pretreatment method is fascinating one which facilitates the removal of lignin, the hydrolysis of hemicellulose and the increase in the surface area for cellulose hydrolysis but still it suffers from a number of problems such as low hemicellulose sugar yield, incomplete disruption of the lignin-carbohydrate matrix (Chiaramonti et al., 2012) and generation of degradation products like furfural, hydroxymethylfurfural (Martin-Sampedro et al., 2012) and soluble phenolic compounds that are inhibitory to microbial growth (Jorgensen et al., 2007). Therefore, it is still a problematic option for long-term ethanol production.

3. Acid pretreatment

Acid pretreatment is one of the most popular methods to attain high sugar yields from lignocellulosic biomass (Lee, Li, Lee, Ryu, & Oh, 2013). The main objective of acid pretreatment is to increase the accessibility of the enzymes to the cellulosic fractions by solubilizing the hemicellulosic fraction of the biomass (Alvira, Tomoas-Pejo, Ballesteros, & Negro, 2010; Pedersen, Johansen, & Meyer, 2011). Both dilute and concentrated acids have been employed for the pretreatment of highly complex lignocellulosic materials but the use of concentrated acid is not much attractive as it is toxic, corrosive, hazardous, and requires reactors that need expensive construction materials resistant to corrosion and there is always a risk of the formation of inhibiting compounds (Talebnia et al., 2010). Additionally, the concentrated acid must be recovered and recycled after hydrolysis to make the process economically feasible (Sun & Cheng, 2002; Girio et al., 2010; Zheng et al., 2009). Therefore, as compared to concentrated acid, pretreatment with dilute acid has been found to be more efficient due to use of less severe conditions (Kumar, Singh, & Ghosh, 2009; Kumar, Barrett, Delwiche, & Stroeve, 2009) as well as generation of less degradation compounds (Hendriks & Zeeman, 2009). Moreover, dilute acid pretreatment has also been found to be suitable for a wide range of feedstocks including softwood, hardwood, herbaceous crops, agricultural residues, waste paper and municipal solid waste (Chung, Bakalinsky, & Penner, 2005; Mosier et al., 2005).

Various acids utilized for pretreatment of different lignocellulosics have been reported in the literature including dilute sulfuric acid (Saha, Iten, Cotta, & Wu, 2005; Marzialetti, Olarte, & Sievers, 2008; Ballesteros et al., 2008; Gil, Ferreira, Amaral, Domingues, & Duarte, 2010), dilute nitric acid (Salvi, Aita, & Robert, 2010), dilute hydrochloric acid (Kurakake, Ouchi, Kisaka, & Komaki, 2005), dilute phosphoric acid (Goshadrou, Karimi, & Taherzadeh, 2011), peracetic acid (Zhao, Wang, & Liu, 2007; Zhao, Wang, & Liu, 2008a) and dilute oxalic acid (Scordia, Cosentino, Lee, & Jeffries, 2011). Among all these, the most widely exploited and tested approach is based on dilute sulfuric acid because it is low-cost, highly active and readily available chemical for industrial applications along with low safety and environmental concerns (Karimi, Emtiazi, & Taherzadeh, 2006; Agbogbo & Wenger, 2006; Wang, Lee, Zhu, & Jeffries, 2011; Chandel, Chandrasekhar, Konakalla, Rudravaram, & Pogaku, 2011). The dilute sulfuric acid was also found to achieve high yields of xylose from xylan, which could not only eliminate the need for xylanase enzymes (Lloyed & Wyman, 2005; Sousa et al., 2009) but also increased the enzymatic cellulose digestibility (Tucker, Kim, Newman, & Nguyen, 2003; Taherzadeh & Karimi, 2008; Kumar, Barrett et al., 2009). However, Kootstra, Beeftink, Scott, and Sanders (2009) reported that less amount of inhibitory furfural was formed in the presence of maleic and fumaric acid pretreatments as compared to sulfuric acid. Interestingly, the bioconversion efficiency was found to be dwindled at higher temperatures in the presence of dilute acids by the degradation of xylose to byproducts such as furfurals which start acting as the fermentation inhibitors (Lee, Zhu, Scrdia, & Jeffries, 2011; Qin, Liu, Li, Dale, & Yuan, 2012; Dagninoa, Chamorro, Romano, Felissia, & Area, 2013). Therefore, dilute acid pretreatment conditions of temperature, time and acid concentration (Table 1) need to be optimized for the recovery of maximum yield of reducing sugars. Corroborating with this, a dilute acid pretreatment at 170 °C was stated to be very much optimum for maximizing total sugar yield (Kim, 2011; Wang et al., 2011; Lee et al., 2011).

Although the efficiency of subsequent cellulose conversion to sugar by enzymatic hydrolysis is greatly increased by dilute acid pretreatment but it does not fully remove lignin which is supposed to precipitate on the cellulose surface and inhibit the hydrolysis process through a combination of binding with the cellulase enzymes and blocking the progress of the enzymes along the glucose chains (Zhang & Lynd, 2004). Hence, it would be beneficial to remove or modify lignin in a way that reduces its negative influence on enzymatic hydrolysis and promote enzymatic digestibility

Table 1
Optimum conditions for dilute sulfuric acid pretreatment.

Temp. (°C)	Time (Min.)	Acid used (%)	Maximum sugar (%)	Xylose yield (%)	Glucose yield (%)	References
170	30	2.2	88	75	97	Wang et al. (2011)
170	30	1.65	–	55	–	Lee et al. (2011)
		0.8	–	–	75	Lee et al. (2011)
140	30	1.2	94	83	–	Redding, Wang, Keshwani, and Cheng (2011)
120	10	3.0	–	76.41	50.04	Phuengjayaem and Teeradakorn (2011)
120	43	2.0	–	77	8.4	Lu, Zhang, Yang, and Liang (2007)
121	60	1.2	70	–	–	Sun and Cheng (2005)
180	15	0.5	76	–	–	Saha et al. (2005)
160	40	0.5	–	93.1	11.8	Shen and Wyman (2011)
123	90	1	–	87.2	–	Cai, Ge, Ling, Cheng, and Ping (2012)
125	30	0.5	–	–	78.1	Cai et al. (2012)
120	60	1.0	75	–	–	Volynets and Dahman (2011)
140	40	1.0	86 (glucose + xylose)	–	–	Shi, Ebrik, and Wyman (2011)
147	30	1.53		69	26	Baboukani, Vossoughi, and Alemzadeh (2012)

of lignocellulosic materials. For the same purpose, Qing, Yang, and Wyman (2010) studied the effectiveness of some surfactants, viz., Tween-80, dodecylbenzene sulfonic acid and polyethylene glycol 4000 (PEG 4000), as additive for pretreatment of corn stover biomass with dilute acid at 140–220 °C and evaluated that all of these surfactants enhanced lignin removal and also improved cellulose digestibility by increasing the hydrophobicity of the biomass so that the hydrolytic enzymes could become easily accessible to the cellulosic fraction. Similar results were also indicated for Tween-20 added during dilute acid pretreatment of wheat straw biomass (Qi, Chen, & Wan, 2010). Therefore, all these facts make the additive surfactants quite better option for acid pretreatment (Kumar & Wyman, 2009a) but Satyanagalakshmi et al. (2011) found that X-100 was most effective among Tween-80, Triton X-100 and PEG.

For improving the pretreatment of lignocellulosic biomass, dilute acid can also be combined with other pretreatment methods. Some of the studies have shown that when acids are combined with alkali, they play a more effective role in lignocellulosic waste pretreatment than acid and alkalis alone (Damisa, Ameh, & Umoh, 2008; Kim, Park, Seo, & Kim, 2012). The combination of acid and alkaline pretreatments (strong acid–strong alkali or weak acid–weak alkali) removed most of the non-cellulosic materials, making cellulose more accessible to the enzymes which convert it into fermentable sugars (Zhang, Shahbazi, & Wang, 2010a). Sulfuric acid and ammonium hydroxide have been studied for effective hemicellulose and lignin removal, respectively (Jeong, Um, Kim, & Oh, 2010). Kim (2011) investigated a two-stage process in which an extremely low acid percolation process and the ammonia recycle percolation (ARP) were operated in series. He recovered hemicellulose in the first stage using sulfuric acid and lignin in the second stage using ammonium hydroxide which resulted in pure cellulose fiber production.

Although dilute acid pretreatment can significantly improve the cellulose hydrolysis but its cost is usually higher than some other physico-chemical pretreatment processes like steam explosion or ammonia fiber expansion (Mosier et al., 2005). Simultaneously, some more limitations/disadvantages faced by dilute acid pretreatment are:

1. Corrosion that mandates expensive materials of construction (Brodeur et al., 2011).
2. Neutralization of the acidic prehydrolysates before the sugars proceed to fermentation (Donghai, Junshe, Ping, & Yanping, 2006; Zhu & Pan, 2010).
3. Gypsum has problematic reverse solubility characteristics when neutralized with inexpensive calcium hydroxide (Mosier et al., 2005).
4. Formation of degradation products and release of natural biomass fermentation inhibitors (Martin, Almazan, Marcet, & Jonsson, 2007; Mehmood et al., 2009).
5. The price of acids has increased tremendously so that the economic feasibility of dilute acid pretreatment might need to be reconsidered (Zheng et al., 2009; Liang, Yoshida, & Uryu, 2013).

The results of Zhang and Lynd (2004) and Weiss, Farmer, and Schell (2010) suggested that hot dilute sulfuric acid pretreatment of biomass increased enzymatic digestibility not only through lignin redistribution as distinct aggregates rather than forming a coating on cellulose fibrils but also through dissolution of the hemicelluloses as it increased porosity and improved enzymatic digestibility. The researchers have also reported the side-effect of hemicelluloses removal and hydrothermal conditions as it might be annealing cellulose that could have increased crystallinity and limited the efficiency of this pretreatment method (Kumar, Barrett et al., 2009; Pingali et al., 2010; Li et al., 2010).

4. Alkaline pretreatment

Among the various chemical pretreatments, alkali pretreatment is the most widely used method to enhance the enzymatic hydrolysis of various lignocellulosic biomasses. Sodium, potassium, calcium and ammonium hydroxides are the frequently used reagents for the alkaline pretreatment. Among these, sodium hydroxide (NaOH) has received the greatest attention due to its outstanding delignification capacity which is essential to achieve high biomass digestibility (McIntosh & Vancov, 2010; Silverstein, Chen, Sharma-Shivappa, Boyette, & Osborne, 2007; Binod et al., 2012), high reaction rate (Cui, Jian, Wan, & Li, 2012), high ethanol production and non-production of any inhibitory material (Shaibani, Ghazvini, Andalibi, & Yaghmaei, 2011). As compared with nitric and sulfuric acids, 3% sodium hydroxide was found to be more effective pretreatment agent to enhance the enzymatic saccharification (Rashid, Alam, Karim, & Salleh, 2011) because dilute NaOH treatment might have caused lignocellulosic biomass to swell leading to an increase in the internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates and disruption

of the lignin structure (Taherzadeh & Karimi, 2008; Damisa et al., 2008; Agbor, Cicek, Sparling, Berlin, & Levin, 2011; Ibrahim, El-Zawawy, Abdel-Fattah, Soliman, & Agblevor, 2011). However, between sodium hydroxide and calcium hydroxide, pretreatment with calcium hydroxide was found preferable as it was less expensive, more safer (Chen, Chen, & Wang, 2012) and could be easily recovered from the hydrolysates by reaction with carbon dioxide (Mosier et al., 2005; Rabelo, Fonseca, Andrade, Maciel Filho, & Costa, 2011). Calcium hydroxide pretreatment also improved biodegradability especially for high lignin content substrates (Fernandes, Klaasse Bos, Zeeman, Sanders, & Van Lier, 2009).

Investigations show that the effectiveness of alkaline pretreatment depends on the substrate and treatment conditions. In general, alkaline pretreatment is more effective on hardwood, herbaceous crops and agricultural residues with low lignin content than on softwood with high lignin content (Deejing & Ketkorn, 2009; Galbe & Zacchi, 2012). Alkaline pretreatment with sodium hydroxide under mild operating conditions resulted in significant reduction of hemicellulose (Chaudhary, Singh, & Ghosh, 2012) and the crystallinity of cellulose, which might be responsible for improved enzymatic hydrolysis (Mirahmadi, Kabir, Jeihanipour, Karimi, & Taherzadeh, 2010; Bahcegul, Toraman, Ozkan, & Bakir, 2012). The results of Zhu, Wan, and Li (2010) indicated that sodium hydroxide pretreatment could preserve most of the carbohydrates but caused substantial lignin degradation during 24 h pretreatment at room temperature. Wang, Keshwani, Redding, & Cheng (2008) reported that sodium hydroxide was more efficient than calcium hydroxide at 121 °C for high reducing sugars yield after enzymatic hydrolysis. Eventually, 121 °C was found to be an impractical temperature to sustain coupled with a pressure of 15 psi from a large scale industry point of view, thereby, alkaline pretreatment at room temperature seemed to be the best method to be followed (Liu, Wang, Han, & Niu, 2012).

Wu et al. (2011) evaluated the effect of alkaline pretreatment at low temperatures to make cellulose more accessible to hydrolytic enzymes. When pretreatment was conducted under freezing conditions (−15 °C) with sodium hydroxide and urea, about 80% theoretical xylose yield and 60% mannose yield were obtained (Zhao, Wang, Zhu, Ragauskas, & Deng, 2008b), somehow, this amount of sodium hydroxide and urea used in this study were too high for actual industrial applications. To solve these problems, several approaches including sodium hydroxide recovery, partial sublimation of sodium hydroxide either by using black liquor from kraft pulping or calcium hydroxide may be used. But still it is difficult to lower the operation temperature in a large scale industrial operation. The supplement of sodium sulphite (Na_2SO_3) in alkali pretreatment could facilitate delignification and significantly improved the enzymatic saccharification (Li et al., 2012). The addition of hydrogen peroxide (H_2O_2) in sodium hydroxide treatment minimized the endwise hydrolysis of hemicelluloses, which acted as the primary pathway for sugar degradation (Gupta & Lee, 2010). Combination of sodium hydroxide and calcium hydroxide effectively reduced the chemical expense due to low loading and cost, respectively (Xu & Cheng, 2011).

Although alkaline pretreatment is more efficient in solubilization of lignin but have little effect on the solubilization of cellulose and hemicelluloses (Girio et al., 2010). A significant disadvantage of alkaline pretreatment is the conversion of alkali into irrecoverable salts or the incorporation of salts into the biomass during the pretreatment reactions making the alkaline pretreatment a challenging issue (Hendriks & Zeeman, 2009).

In comparison with other pretreatment technologies, alkali pretreatment effectively removed most of the lignin (Dawson & Boopathy, 2008; Singh & Bishnoi, 2013; Monlau, Barakat, Steyer, & Carrere, 2012) and a part of hemicelluloses. It also increased the digestibility of cellulose usually at less severe conditions such as lower temperature and pressures, even ambient conditions, although longer pretreatment times were required (Carvalheiro, Duarte, & Girio, 2008; Zhang, Wang, Su, Qi, & He, 2010b). As compared to acid processes, alkaline pretreatment resulted in less degradation of sugars (Verga, Szengyel, & Reczey, 2002; Kumar & Wyman, 2009b). The results of Copur, Tozluoglu, and Ozkan (2013) also showed that the highest glucan to glucose conversion (74.4%) and the highest ethanol yield (52.6 g/kg husks) were observed for hazelnut husks treated with 2% sodium hydroxide for 90 min. The mechanism of alkaline pretreatment is believed to be the solvation and saponification of intermolecular ester bonds cross-linking xylan, lignin and other hemicelluloses. The solvation and saponification cause the removal of these cross-links and enhance the porosity of the lignocellulosic materials (Laureano-Perez, Teymouri, Alizadeh, & Dale, 2005; Hendriks & Zeeman, 2009; Leustean, 2009). Alkali pretreatment also removes acetyl and various uronic acid substitutions on hemicellulose that increase the accessibility of hemicellulose as well as cellulose to enzymes (Chang & Holtzapple, 2000; Yang et al., 2012).

5. Conclusion

Lignocellulosic biomass is a tough feedstock owing to the compact packing of its components, viz., cellulose, hemicelluloses and lignin. Pretreatment is always required to break this compact structure to make cellulose accessible for efficient enzymatic hydrolysis. Feasibility of three different pretreatment methods (Steam explosion, acid and alkaline) has been discussed with reference to their applicability, cost and environmental point of view. Based upon the literature studies, each method has its own advantages and disadvantages. Albeit, on the basis of feedstock types, geographical conditions and availability of technology, the appropriate method can be selected and used but to make these processes more cost effective and efficient, further research for technological advancement is highly recommended.

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