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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