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Microwave-assisted alkalic salt pretreatment of corn cob wastes: Process optimization for improved sugar recovery

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ABSTRACT

The present study developed three different microwave-assisted alkalic salt pretreatments ($Na_3PO_4 \cdot 12H_2O$, Na_2CO_3 and CH_3COONa) to improve sugar yield from corn cob wastes. Process inputs included pretreatment time, alkalic salt concentration and microwave power intensity with the sugar yield as the corresponding output. All three pretreatment models gave high coefficient of determination values ($R^2 > 0.85$). The $Na_3PO_4 \cdot 12H_2O$ treatment (11.55% $Na_3PO_4.12H_2O$ at 700 W for 6 min) led to the maximum sugar yield (0.76 ± 0.01 g/g). All three pretreatment methods displayed key structural changes in the corn cob structure after pretreatment. This study gave an 11% higher sugar yield in contrast to a previous microwave-assisted pretreatment report on corn cobs. The developed pretreatment strategy was effective for improving the sugar recovery from lignocellulosic wastes and can be channelled towards microbial production of fuels and high value commodities.

1. Introduction

Lignocellulosic material lends itself as a potential substrate for biofuel production and high-value bioproducts since it is cost-effective and abundant. The major constituents of lignocellulosic waste include lignin (15–25%), cellulose (38–50%) and hemicellulose (23–32%) (McKendry, 2002). Various lignocellulosic type substrates are being investigated. Some examples include corn wastes (Potumarthi et al., 2012; Saha et al., 2013), sugarcane wastes (Moodley and Gueguim Kana, 2017a; Ramadoss and Muthukumar, 2015), rice straw (Yang et al., 2012), sorghum leaves (Rorke et al., 2017) and wheat straw (Jin et al., 2013). Annually, the production of corn surpasses 1 billion metric tons and this contains the stalks, cobs, leaves and husks (USDA, 2017). From the aforementioned corn wastes, the cobs are promising for biofuel production processes due to its high energy density (4960–5210 MJ/kg) compared to other feedstocks (corn stover and switchgrass) (Potumarthi et al., 2012).

However, recalcitrant layers (lignin moeties) present within the lignocellulosic matrix makes the glucose-rich cellulose polymer inaccessible to enzymatic hydrolysis and microbial cultures. Therefore, the application of lignocellulosic-type substrates for microbial production of fuels and high value commodities requires efficient chemical pretreatment methods to degrade the resistant structures. The unravelling of these components will significantly improve the saccharification process, yielding high sugar that can be utilized for microbial fermentations (Kang et al., 2013).

Chemical lignocellulosic pretreatments are rapidly developing on a global scale with acid and alkaline methods as the gold standard (Aguilar-Reynosa et al., 2017). Despite the availability of previous lignocellulosic biomass pretreatment reports, their potential industrially is hindered by high cost and energy intensive processes, low fermentable sugar yields and the formation of toxic by-products such as fermentation inhibitor compounds. On-going studies are being focused on high efficiency, low-cost lignocellulosic pretreatment methods.

Alkalic salts have garnered significant interest as suitable replacement catalysts for alkaline pretreatments (Sewsynker-Sukai and Gueguim Kana, 2017). Previously investigated salts include Na_2CO_3 (Qing et al., 2016b), Na_3PO_4 (Sewsynker-Sukai et al., 2018; Qing et al., 2016b), and Na_2S (Qing et al., 2016a). Chemical reaction mechanisms of these alkalic salts are similar to strong alkaline-based methods such as NaOH. Alkalic salt pretreatments cause swelling of the biomass fibres and increases porosity which facilitates the diffusion of hydrolytic enzymes, thus enhancing sugar recovery (Sewsynker-Sukai and Gueguim Kana, 2017). Additionally, they cause lignin and hemicellulose disbanding, the removal of ester bonds, the rearrangement and modification of lignin fragments and cellulose crystallinity (Kim et al., 2016).

Previous pretreatment reports have coupled alkalic salts with conventional steam-assisted heating (Sewsynker-Sukai and Gueguim Kana, 2017; Sewsynker-Sukai et al., 2018; Qing et al., 2016a,b). The study by

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Table 1
Experimental runs for the MAAS pretreatments.

Run Order	Salt conc. (%)	Power (W)	Pretreatment time (min)	Reducing sugar yield (g/g)		
				CH_3COONa	Na_2CO_3	$Na_3PO_4.12H_2O$
1	7.5	0	8	0.26	0.36	0.39
2	7.5	400	5	0.35	0.58	0.67
3	15	400	2	0.33	0.44	0.59
4	7.5	0	2	0.31	0.16	0.39
5	7.5	400	5	0.33	0.58	0.73
6	15	0	5	0.32	0.33	0.40
7	0	0	5	0.31	0.31	0.31
8	15	800	5	0.39	0.69	0.71
9	7.5	400	5	0.33	0.62	0.68
10	7.5	400	5	0.33	0.63	0.72
11	7.5	800	8	0.43	0.65	0.71
12	0	800	5	0.32	0.32	0.32
13	7.5	400	5	0.36	0.64	0.69
14	0	400	8	0.34	0.34	0.34
15	15	400	8	0.31	0.68	0.71
16	0	400	2	0.31	0.31	0.32
17	7.5	800	2	0.28	0.44	0.49

Note: g/g = g reducing sugar/ g dry weight corn cobs.

Sewsynker-Sukai and Gueguim Kana (2017) optimized a sequential $Na_3PO_4.12H_2O$ and $ZnCl_2$ method for enhanced enzymatic digestibility from corn cobs. Likewise, Qing et al. (2016b) screened various alkalic salts (CH_3COONa, Na_2CO_3, $Na_3PO_4{\cdot}12H_2O$, NaClO, $Na_3C_6H_5O_7.2H_2O$ and $Na_2MoO_4.2H_2O$) combined with H_2O_2 for improved enzymatic saccharification of bamboo shoot shell. Similarly, Gong et al. (2015) developed a H_2O_2-assisted Na_2CO_3 pretreatment using corn stover.

Microwave irradiation has appeared as a highly efficient heating mechanism for the enhancement of lignocellulosic degradation (Aguilar-Reynosa et al., 2017). Heat propagation mechanisms using microwave irradiation includes (1) ionic conduction and (2) bipolar rotation. Ionic conduction occurs when available free ions or ionic species are orientated using motions produced in the electric field and triggers rapid heating. Denser solutions create more shocks which converts more kinetic energy. On the other hand, the bipolar rotation mechanism refers to interactions in which polar molecules are quickly arranged in a straight single line. Friction as a result of the molecules rotation produces energy that is transmitted to heat (Aguilar-Reynosa et al., 2017). The polarity and dielectric properties of the molecules influence the ability to achieve bipolar rotation (Sosa-Morales et al., 2010; Singh and Bishnoi, 2012; Yin, 2012). The proficient storage of electrostatic energy when an electric field is present is referred to as a dielectric property. Dielectric properties are crucial during microwave heating because dielectric type materials are polarized in the presence of an electrical field and possess beneficial electromagnetic interaction (Stuerga, 2006). Microwave irradiation makes use of dielectric polarization to degrade the resistant lignocellulosic components. Additionally, it generates thermal heat zones that accelerate the colliding of ions and leads to rapid rotation of dipole molecules. This process raises the temperature at shorter times (Alvira et al., 2010; Farag et al., 2012).

Due to these characteristics, microwave irradiation is considered more effective for a higher heating efficiency compared to conventional steam heating such as autoclave and water bath methods (Zhu et al., 2016). The study by Moodley and Gueguim Kana (2017a) reported a 49% increase in sugar yield from sugarcane leaf wastes using a microwave-assisted NaOH-based pretreatment compared to autoclave heating. Likewise, Hu and When (2008) observed a 53% enhancement in sugar yield from NaOH pretreated switchgrass using microwave heating compared to a steam-assisted method. Microwave irradiation proposes several benefits compared to conventional steam heating methods that include: (a) shorter pretreatment reaction time, (b) faster heat transfer, (c) energy and cost efficient, (d) direct heating that prevents overheating of surfaces, and (e) is environmentally benign (Farag et al., 2012; Aguilar-Reynosa et al., 2017; Moodley and Gueguim Kana, 2017a). Microwave pretreatment of lignocellulosic biomass has recently attracted considerable attention as an effective heating mechanism (Aguilar-Reynosa et al., 2017). However, there is a paucity of knowledge on the effect of alkalic salts combined with microwave heating.

Therefore, this study developed three different microwave-assisted alkalic salt (MAAS) pretreatments (CH_3COONa, Na_2CO_3 and $Na_3PO_4.12H_2O$) for improved sugar yields from corn cob waste. In addition, the influence of the developed MAAS pretreatment methods on the corn cob structure was examined.

2. Materials and methods

2.1. Materials

The substrate was retrieved, dried and ground according to Sewsynker-Sukai and Gueguim Kana (2017). The compositions of the native and optimally pretreated corn cob samples were analysed following the methodology by Sluiter et al. (2008). The Cellic CTec 2 enzymes (160 FPU/ml) were kindly donated by Novozymes (Novozymes A/S, Denmark). The enzymatic activity was calculated according to Sewsynker-Sukai and Gueguim Kana (2018).

2.2. Microwave-assisted alkalic salt pretreatment

The microwave-assisted alkalic salt (MAAS) pretreatments were performed with a microwave oven (Samsung, ME9114S1). Different alkalic salts (CH_3COONa, Na_2CO_3 and $Na_3PO_4.12H_2O$) were investigated. Response Surface Methodology (RSM) (Box-Behnken design) models were used for optimization. The pretreatment input parameters consisted of alkalic salt concentration (0–15%, w/v), microwave power intensity (0–800 W) and microwave pretreatment time (2–8 min) while the output was the reducing sugar yield (Table 1). These parameter ranges were chosen following an extensive literature survey (Qing et al., 2016b; Kaur and Phutela, 2016; Moodley and Gueguim Kana, 2017b). A solid loading of 10% (w/v) was used for all experiments (Table 1). The pretreated substrate was filtered and washed using the methods adopted by Sewsynker-Sukai et al. (2018).