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A sustainable and effective potassium hydroxide pretreatment of wheat straw for the production of fermentable sugars

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ABSTRACT

The development of sustainable and effective pretreatment technology is of critical importance for the conversion of lignocelluloses into bioethanol. In this work, KOH pretreatment of wheat straw with the supplement of anthraquinone (AQ) and sodium lignosulfonate (SLS) was investigated under the relatively mild conditions. The effectiveness of KOH pretreatment was evaluated by enzymatic saccharification. It was found that after the KOH pretreatment with 15% KOH, 0.1% AQ and 2% SLS at 120 °C for 40 min, the final total sugar yields (glucose + xylose + soluble xylan) could reach up to 80%, which was 16% higher as compared to the KOH pretreatment without addition of AQ and SLS under the same conditions. In addition, the spent liquor could be reused twice to maintain a relatively good effectiveness of pretreatment, and it could be used to produce fertilizer due to the high content of potassium.

1. Introduction

The development of sustainable and renewable energy alternatives has been gaining a lot of popularity due to increased energy demand leading to the reduction in the usage of fossil fuels (Xu et al., 2016). Particularly, bioethanol produced from lignocelluloses has been extensively studied in the past decades (Li et al., 2017), because it has been known that the blending of bioethanol in vehicle gasoline can significantly reduce carbon emission (Ozdingis and Kocar, 2017; Ragauskas et al., 2014). The United States and Brazil are the pioneers in the usage of ethanol gasoline. Most recently (Sep. 13th, 2017), 15 departments of Chinese government (including the National Development and Reform Commission, the National Energy Administration, etc.) jointly issued "the Implementation Plan of Expanding the Production of Biofuel Ethanol and Promoting the Utilization of Ethanol Gasoline in Vehicles", which explicitly put forward that the nationwide promotion of the use of ethanol gasoline for motor will basically achieve full coverage by 2020, and cellulosic ethanol is striving to achieve large-scale commercial production by 2025 in China.

However, the production of cellulosic ethanol requires sustainable and cost-effective pretreatment technology to break the strong barrier (i.e. natural recalcitrance, like the presence of lignin and the high crystallinity of cellulose) of lignocelluloses for the efficient downstream production of fermentable sugars (Ding et al., 2012). Among various physical, chemical, biological, and the combined pretreatment approaches, alkali-based pretreatment (mostly, NaOH is used) is one of the most promising technologies, because it can efficiently remove lignin, obtain high final total sugar yields, and generate less inhibitors, in comparison with hydrothermal pretreatment and dilute acid pretreatment (Sun et al., 2014). On the other hand, alkali-based pretreatment can be integrated with alkali-based pulp mill through the partial utilization of the mature pulping equipment, the well-developed wastewater treatment and chemical recovery systems, to reduce the capital cost (von Schenck et al., 2013).

Yet, in the case of agricultural waste (e.g. wheat straw), the material collection radius is quite limited due to the low density of straw and the high cost of transportation. This actual situation leads to the fact that the production scale of ethanol plant in China will be small (the feedstock throughput of less than 100,000 tons per year). Such small scale of plant could result in a very high capital cost of alkali recovery system including the combustion of black liquor and causticization (Gong et al., 2015). Despite the inexpensive sodium carbonate could be used

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Table 1
Effect of KOH dosage on the pretreatment of wheat straw.

	Raw materials	15%KOH, L/S = 6				20%KOH, L/S = 6			
		80 °C 180 min	90 °C 90 min	100 °C 60 min	120 °C 40 min	80 °C 180 min	90 °C 90 min	100 °C 60 min	120 °C 40 min
Rsolid/%	–	46.98 ± 0.19	50.48 ± 0.22	48.30 ± 0.25	52.90 ± 0.22	44.45 ± 0.59	45.25 ± 0.41	42.48 ± 0.35	41.70 ± 0.55
Glucan/%	30.04 ± 0.06	49.21 ± 0.47	51.2 ± 0.38	50.51 ± 0.72	51.10 ± 0.61	52.78 ± 0.38	48.50 ± 0.42	50.14 ± 0.34	52.99 ± 0.64
Xylan/%	18.23 ± 0.03	14.81 ± 0.16	14.60 ± 0.24	16.75 ± 0.37	18.63 ± 0.22	15.48 ± 0.26	15.33 ± 0.58	14.56 ± 0.55	20.75 ± 0.71
Lignin/%	23.63 ± 0.17	6.80 ± 0.28	8.14 ± 0.11	7.86 ± 0.19	6.73 ± 0.23	8.18 ± 0.08	7.08 ± 0.09	6.47 ± 0.10	6.71 ± 0.12
D_{lignin}/%	–	86.47 ± 0.58	82.61 ± 1.02	83.93 ± 0.95	84.93 ± 0.78	84.61 ± 0.69	86.44 ± 0.75	88.36 ± 0.82	88.16 ± 0.79
R_{glucan}/%	–	76.96 ± 0.81	86.04 ± 0.56	81.21 ± 0.61	89.99 ± 0.82	78.10 ± 0.64	73.06 ± 0.86	70.91 ± 0.67	73.56 ± 0.63
R_{xylan}/%	–	38.17 ± 0.75	40.43 ± 0.39	44.37 ± 0.81	54.06 ± 0.79	37.74 ± 0.61	38.05 ± 0.91	33.94 ± 0.82	47.46 ± 0.91

as an alternative to NaOH and its recovery does not need causticization, its weak basicity results in a less effectiveness of pretreatment. The addition of chemicals like O_2 (Arvaniti et al., 2012; Geng et al., 2014), Na_2S (Gu et al., 2012), Na_2SO_3 (Yang et al., 2012), or H_2O_2 (Gong et al., 2015) could ameliorate lignin removal, promoting enzyme accessibility during saccharification, but this approach could in turn increase the process cost or result in environmental problems if the spent liquor contains sulfur and the mill scale is small (Yang et al., 2012). $Ca(OH)_2$ or NH_3 can also be used to do alkaline pretreatment, but the calcium precipitation has to be well addressed (Zhang et al., 2014), and the stench of NH_3 could impact environment (Xu et al., 2016). Therefore, the development of sustainable and cost-effective pretreatment technology is of critical importance for the clean production of fermentable sugars and cellulosic ethanol.

Potassium hydroxide (KOH) as a strong base could also be used in alkali pretreatment for different feedstocks (Liu et al., 2015; Sun et al., 2014), and it has been verified that the spent liquor containing potassium could be used for the production of fertilizer (Jahan and He, 2018; Muhammad et al., 2016). However, like NaOH, KOH could also cause much degradation of hemicellulose (even over 30%), resulting in the loss of fermentable sugars (Li et al., 2013). To overcome this issue, in this work, anthraquinone (AQ) was used as a reagent to assist KOH pretreatment because AQ could stabilize carbohydrates and simultaneously promote lignin removal (Xu et al., 2015). On the other hand, well penetration of insoluble AQ in the initial stage of alkali pretreatment is of importance for the homogeneous treatment of feedstock, although the active form of AQ (anthrahydroquinone (AHQ)) is soluble in water (Hart and Rudie, 2014). Thus, surfactant could be used to promote chemical penetration and the dissolution of AQ (Cao and Aita, 2013). In this study, sodium lignosulfonate (SLS) was chosen as another reagent because SLS is an inexpensive surfactant and it does not cause bubble issues during pretreatment (Xu et al., 2015). The effectiveness of KOH-based pretreatment was evaluated by enzymatic saccharification following the standard National Renewable Energy Laboratory (NREL) protocol. The property changes of wheat straw before and after pretreatment were characterized by chemical composition analyses, Fourier Transform Infrared Spectroscopy (FTIR) investigation, X-ray diffraction (XRD) tests, scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS) observation, etc. In addition, the mass balance of pretreatment and saccharification was discussed.

2. Materials and methods

2.1. Materials

The wheat straw used in this study was obtained from Dingyuan, Anhui Province, China. The air-dried wheat straw (moisture content was less than 10%) was milled with a twin screw extrusion system (maximum feedstock throughput was 200 kg/h) to reduce particle size, as reported previously (Liu et al., 2013). Then, the milled wheat straw was stored in a sealed bag at 4 °C refrigerator to uniformize the moisture content.

The enzyme used for enzymatic hydrolysis was cellulase with the enzymatic activity of 60 filter paper units/mL (FPU/mL) provided by Qingdao Vland Biotech Inc. All the used chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. in China and used as received without further purification.

2.2. KOH pretreatment of wheat straw

The pretreatment process was carried out in a cooking digester (VRD-42SD-A China Pulp and Paper Research Institute, Beijing, China). The cooking digester consisted of four small cooking pots with a volume of 1 L of each. 50 g wheat straw (oven dried) was added in each small cooking pot. Potassium hydroxide (KOH), sodium lignosulfonate (SLS) and anthraquinone (AQ) were used as cooking agents. The pretreatment conditions like the pretreatment temperature, cooking time, liquid-to-solid ratio and the dosage of additives are shown in Tables 1, 2 and 3. Upon completion of pretreatment, the small cooking pots were cooled down with tap water immediately. The spent liquor was squeezed out and the pretreated wheat straw samples were washed with tap water (10 times volume of spent liquor) to remove dissolved lignin and residual chemicals. After that, the pretreated wheat straw and spent liquor were stored at 4 °C for further analysis. For the study of the reuse of spent liquor, a certain amount (200 mL) of black liquor was added to the next batch of pretreatment at the same cooking conditions. For

Table 2
Effect of the additives on the pretreatment of wheat straw.

	Raw materials	15%KOH, 80 °C, 120 min, L/S = 6			
		–	0.1%AQ	2%SLS	0.1%AQ + 2%SLS
Rsolid/%	–	46.06 ± 0.32	46.81 ± 0.45	50.47 ± 0.30	50.01 ± 0.42
Glucan/%	30.04 ± 0.06	54.85 ± 0.38	56.75 ± 0.44	55.09 ± 0.31	57.87 ± 0.33
Xylan/%	18.23 ± 0.03	22.81 ± 0.36	21.67 ± 0.32	21.4 ± 0.24	23.03 ± 0.20
Lignin/%	23.63 ± 0.17	10.46 ± 0.02	9.16 ± 0.06	10.15 ± 0.08	7.65 ± 0.06
Extractives%	29.05 ± 0.32	9.91 ± 0.33	7.40 ± 0.22	12.38 ± 0.24	8.75 ± 0.36
D_{lignin}/%	–	79.61 ± 0.38	81.85 ± 0.30	77.95 ± 0.31	83.79 ± 0.28
R_{glucan}/%	–	84.13 ± 1.15	88.43 ± 1.52	92.56 ± 1.06	96.34 ± 1.34
R_{xylan}/%	–	57.63 ± 1.30	55.64 ± 1.35	57.97 ± 1.02	63.18 ± 1.08