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ORIGINAL RESEARCH

Different acid pretreatments at room temperature boost selective saccharification of lignocellulose via fast pyrolysis

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Abstract Fermentable sugars are a group of pivotal intermediates and platform compounds achieved by the conversion of lignocellulose. Fast pyrolysis, as a little-explored way to liberate levoglucosan from biomass, may have a potential capability to overcome the technical barriers and fundamental limitations for efficient saccharification. Pretreatment prior to fast pyrolysis is essential to improve levoglucosan yield from lignocellulose. Contrary to typical high-temperature acid pretreatments, a pretreatment under mild conditions was evaluated and optimized, where different acid (formic acid, acetic acid, oxalic acid, nitric acid, phosphoric acid, sulphuric acid and hydrochloric acid) were employed at room temperature prior to fast pyrolysis of lignocellulose. Due to the alteration of chemical compositions and physical structures of biomass, especially the elimination of alkali and alkaline earth metals, the levoglucosan yield of dilute acid pretreated biomass was improved remarkably as compared with that of raw material, meanwhile claimed that acid pretreatments at room temperature had an enough capability in efficient utilization of biomass. In sum, this study offered a novel and economical strategy for selective saccharification of lignocellulose for industrialized biorefinery.

Keywords Pyrolysis · Acid pretreatment · Levoglucosan · Lignocellulose

Introduction

Lignocellulosic biomass possessing a range of excellent properties has received considerable attention for the production of energy, especially for large-scale manufacturing of fermentable sugars (Jiang et al. 2019a). Fermentable sugars are regarded as easily utilizable intermediates for production of biofuels or other commodity chemicals. In structure, unbranched

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cellulose consists of abundant glucose units joined by β-1,4-glycosidic linkages, and plenty of inter- and intra-strand hydrogen bonds are formed due to a large amount of hydroxyl (OH) groups in glucose units, which leads to a typical rigid and crystalline structure (Jiang et al. 2019b). Since that, it is difficult to overcome the recalcitrance of cellulose structure and the hindrance of complicated components existing parallel to cellulose in the transformed access to fermentable sugars. In a long period, enzymatic saccharification has been universally recognized as a sustainable and well-known approach to releasing fermentable sugars from lignocellulose (Jiang et al. 2016a). Several varieties of enzymes with complementary activities are required in enzymatic saccharification of biomass, and long-chain polymer is needed to be initially broken down into oligosaccharide and then cleaved into monosaccharide during an enzymatic saccharification process. Likewise, enzymatic saccharification has several disadvantages, such as high costs of enzymes and slow rates of saccharification, which limit its large-scale application (Jiang et al. 2019b). Instead, acid hydrolysis is regarded as another widely developed approach for saccharification of biomass. The β-1,4-glycosidic bonds are cleaved and cellulose polymers can be depolymerized to glucose units when catalyzed by acids. Nevertheless, low effectiveness in the recycling of acid along with the separation of products and acids, limited the application of acid hydrolysis (Jiang et al. 2017).

Compared with enzymatic saccharification and acid hydrolysis, fast pyrolysis is an emerging and promising substitute technology for fermentable sugars production from biomass (Jiang et al. 2019c; Li et al. 2017). Fast pyrolysis is a thermo-chemical conversion, typically occurred at 450–600 °C in several minutes in the absence of oxygen. Levoglucosan, is the major component contained in pyrolytic syrup of cellulose (Jiang et al. 2019b; Wang et al. 2018). The content of levoglucosan in the pyrolysate can reach up to 80% and the levoglucosan yield is achieved as high as 70.1 wt% from microcrystalline cellulose (Kwon et al. 2007). It has demonstrated that levoglucosan can be used as substrate in fermentation by biocatalysts, giving comparable yields in processes where glucose is extensively converted to ethanol, citric acid, itaconic acid, malic acid, lipid (Jiang et al. 2019a). Fast pyrolysis is a promising alternative to overcome technical obstacles of hydrolysis technology. Primarily, the reaction for pyrolytic saccharificiation (several minutes) is obviously faster than hydrolysis (several hours or even days). Also, expensive enzymes or corrosive acids are redundant in fast pyrolytic saccharification. In addition, a concentrated series of reactions occur in fast pyrolysis rather than diluted reaction system, leading to considerable convenience in obtaining produced syrup at high concentration of fermentable sugars, which is beneficial for following fermentation and final product separation. Overall, fast pyrolysis, due to less essential operations and capital costs, is considered more economically competitive than enzymatic or acid hydrolysis (So and Brown 1999; Zhang et al. 2013).

However, pyrolysate of lignocellulose is a complicated mixture for the lack of product selectivity in pyrolysis process. Compared with pure cellulose, a decent yield of levoglucosan is unexpectedly difficult to be achieved from lignocellulose. Other components naturally existing together with lignocellulose have remarkable negative influence on the formation of levoglucosan, especially alkali and alkaline earth metals (AAEMs) (Wu et al. 2019). Due to the catalyzed formation of coordinate bonds with the oxygen atoms of the glucose ring, AAEMs can hinder the production of levoglucosan and promote pyranose ring scission (Wang et al. 2017; David et al. 2019). Previous researches have investigated the relationship between compositions in natural biomass and the pyrolytic production of fermentable sugars. It has been verified that there was a noticeable increase on the yield of levoglucosan due to efficient delignification, rather than effects caused by quantitative modification of hemicellulose, which achieved similar yields of levoglucosan, gases and char in fast pyrolysis (Zhang et al. 2015). Hence, the effect caused by different content of hemicellulose existing in the natural biomass is not comparable with that of AAEMs. For an efficient enhancement to saccharification and ultimate production of fermentable sugars, removal of AAEMs is considered as significant as delignification while eliminating the composition of hemicellulose can achieve no exploit, which can be achieved by acid pretreatments at room temperature. Several pretreatments for modifying the chemical composition of biomass prior to pyrolysis were also adopted to improve levoglucosan yields, where acid pretreatments of biomass showed an excellent performance (Jiang et al. 2016b, 2015). Despite there are a considerable number of researches showing that acid washing could significantly change the product distribution and increase the selectivity in the production of levoglucosan, basically these processes were carried out at relatively high temperatures. More precisely, flexibilities of acid pretreatments at room temperature on selective saccharification via pyrolysis of biomass have not been systematically investigated on purpose of eliminating the extra energy consumption which increases the cost of biomass pretreatment. So AAEMs removal prior to biomass pyrolysis is the main influencing factor for sugar production, but acid pretreatments at high temperature might be not essential. Herein, influence of pretreatments by different acid at room temperature was further investigated for selective saccharification of lignocellulose via fast pyrolysis. In this paper, formic acid, acetic acid, oxalic acid, nitric acid, phosphoric acid, sulphuric acid and hydrochloric acid were respectively employed on natural biomass at room temperature, then pretreated biomass was further fast pyrolyzed for levoglucosan production.

Materials and methods

Materials

Reed pole (*Phragmites australis*) with a particle size of 0.11–0.18 mm after grinding and sieving was purchased from Hunan Province. Acids were bought from Chuandong Chemical Co. Ltd., Chongqing. The other chemical reagents were acquired from Sigma (Shanghai).

Dilute acid pretreatments

Reed pole (5 g) was mixed with dilute acid solution (5 wt%, 50 mL) in a flask. The flasks were placed in a shaker and reacted at 30 °C for 20 h. Then, acid pretreated residue was recovered by filtration and washed with deionized water until neutral, then dried to a constant weight in a freeze dryer (Boyikang Co., Ltd, Beijing). Water-washed pretreatment was used as a control group.

Compositional and elemental analysis

The composition of biomass was detected by the procedure of National Renewable Energy Laboratory (Sluiter et al. 2008). The contents of organic elements were determined by an organic Elemental Analyzer (Vario EL cube, Hanau, Germany). The contents of AAEMs were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Optima 8000, PerkinElmer, USA).

Structural characterization

The X-ray diffractometer was set at 40 kV and 40 mA. Biomass (80 mg) was pressed into a layered container of 40 mm radius and passed through copper radiation ($\lambda = 1.54$) at a scan rate of 0.01° per second through a diffraction angle of 5°–45° (2θ°). The crystallinity index (*CrI*) was obtained by the method of Segal et al. (1959). Fourier transform infrared spectrometry (FTIR) analysis was performed on BRUKER TENSOR 27 (Germany).

Thermogravimetric (TG)

TG were implemented in a Thermogravimetric Analyzer (TGAQ50, TA, USA). Biomass (4–6 mg) were put into alumina crucible, and heated from room temperature to 750 °C. Nitrogen was used as carrier gas at a rate of 20 mL/min.

Fast pyrolysis

Fast pyrolysis was performed on a CDS Pyroprobe 5200 series (CDS Analytical, USA) connected to a Gas Chromatograph/Mass Spectrometer (GC/MS) system (Agilent 7890 Gas Chromatograph, Agilent 7975CMass Spectrometer, Agilent Technologies). Prior to fast pyrolysis, biomass (approximately 300 μg) weighted by a micro-balance (XP6152, METTLER TOLEDO, Germany) with an accuracy of 1 μg was pyrolyzed during each test. The heating rate, residence time and pyrolysis temperature were set at 10 k ms^{-1}, 20 s and 500 °C respectively. The pyrolysis products were transferred to GC injection port from the quartz tube by carrier gas (helium) at a flow rate of 20 mL/min. The interface line between the pyrolyzer and the GC was held at 300 °C to avoid possible condensation of the vapor. The split ratio was

50:1. The cleavage product was chromatographed using an HP-INNO wax capillary column (Agilent 19091 N-133, length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm). The methods for separation and identification were introduced in previous work (Jiang et al. 2019b). Quantification of levoglucosan was performed by a five-point calibration curve. Yield of levoglucosan and relative content of other compounds were calculated as following equations:

$$\text{Levoglucosan yield (wt\%)} = \frac{\text{Mass of levoglucosan}}{\text{Mass of cellulose}} \times 100\% \quad (1)$$

$$\text{Relative content of component} = \frac{\text{Area of a compound}}{\text{Area of all compounds}} \times 100\% \quad (2)$$

Results and discussion

Componential and elemental analysis of biomass

Different varieties of acid (formic acid, acetic acid, oxalic acid, phosphoric acid, nitric acid, sulphuric acid, hydrochloric acid) were impregnated for the pretreatment of reed pole at room temperature. Components of cellulose, hemicellulose and lignin in biomass were analyzed (Table 1). Both raw and pretreated biomass had similar contents of cellulose, hemicellulose and lignin. In previous researches, acid pretreatment at high temperature (e.g. 120 °C) was proved to effectively remove hemicellulose and acid-soluble lignin, resulting in an accumulation of cellulose. In contrast, when acid pretreatments performed at room temperature, the contents of cellulose, hemicellulose and lignin were observed to change slightly.

The elemental analysis of biomass before and after pretreatment is shown in Table 2. The composition of C, H and N in biomass before and after acid pretreatments was modified from 47.9 to 48.7 wt%, 6.2 to 6.0 wt% and 0.03 to 0.04 wt%, respectively, from which indicated that there was no obvious alteration for these elements to be observed. However, these acid pretreatments at room temperature could low the total content of AAEMs in biomass significantly, which was totally reduced from 4203.2 to 560.1 ppm. The presence of AAEMs could increase the formation of char and water during carbohydrates dehydration (Jiang et al. 2019a). Na^+ and K^+ were proved to decrease the levoglucosan production by promoting depolymerization/fragmentation reactions responsible for production of lower molecular weight oxygenates (Liu et al. 2008). Mg^{2+} and Ca^{2+} were proved to suppress the levoglucosan production by promoting the formation of char (Zhu et al. 2016). Compared with K^+, Na^+ and Ca^{2+}, it was more difficult to remove Mg^{2+} due to its lower content in original biomass. What's more, water, formic acid, acetic acid and oxalic acid washings had similar results of total AAEMs from 1115.3 to 1290.8 ppm, whereas the content of K^+, Ca^{2+} and Mg^{2+} varied significantly. After pretreated by formic acid, acetic acid and oxalic acid, the content of K^+ in biomass was lower than these washed with water and similar with other acid pretreatments, but the content of Ca^{2+} and Mg^{2+} was higher than pretreated with other acids.

Table 1 The componential analysis of biomass

Samples	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
Un-pretreated	53.1	18.9	23.5
Water washed	53.1	17.9	23.6
Formic acid pretreated	52.7	16.4	24.2
Acetic acid pretreated	51.6	17.7	25.1
Oxalic acid pretreated	53.7	18.3	24.8
Phosphoric acid pretreated	54.7	17.9	24.1
Nitric acid pretreated	54.1	16.5	25.9
Hydrochloric acid pretreated	56.5	17.8	25.0
Sulphuric acid pretreated	55.1	17.7	24.4

Table 2 The elemental analysis of biomass

Samples	Organic elements (wt%)			AAEMs (ppm)			
	C	H	N	K	Na	Ca	Mg
Un-pretreated	47.9	6.2	0.03	2561.1	1055.8	543.2	43.1
Water washed	47.4	6.0	0.03	151.1	275.7	650.1	38.4
Formic acid pretreated	47.5	6.0	0.03	76.0	276.7	826.9	63.4
Acetic acid pretreated	47.4	6.0	0.03	77.5	274.3	794.5	58.3
Oxalic acid pretreated	47.4	6.1	0.04	79.4	289.6	860.2	61.6
Phosphoric acid pretreated	48.7	6.1	0.02	68.1	280.9	202.2	8.9
Nitric acid pretreated	47.9	6.0	0.01	73.3	291.4	202.2	30.1
Hydrochloric acid pretreated	47.9	6.1	0.02	69.5	279.1	237.3	11.3
Sulphuric acid pretreated	47.9	6.0	0.04	64.2	264.7	416.3	22.3

Structural characterization of biomass

Crystallinity of acid-pretreated biomass was characterized (Fig. 1). The *CrI* values of acid-pretreated biomass were increased compared with original biomass, as calculated in biomass pretreated with formic acid, acetic acid, oxalic acid, phosphoric acid, nitric acid, hydrochloric acid, sulphuric acid were 56.4%, 57.8%, 58.4%, 56.7%, 58.7%, 60.7% and 59.4%, respectively. The highest *CrI* (60.7%) was achieved in biomass pretreated by hydrochloric acid. Both the variation and increase in *CrI* was considered principally due to an effective removal of amorphous cellulose and hemicellulose, resulting in higher *CrI* by accumulation of crystalline cellulose. Additionally, crystallinity played a great role in pyrolysis reactions of biomass, considered as one of the leading factors which restricted the distribution of pyrolytic products. Higher *CrI* was deemed relative to a greater levoglucosan production from natural biomass, which could be explained as crystalline cellulose contributed to a formation of levoglucosan during biomass pyrolysis while amorphous cellulose enhanced the productions of coke and gas (Hosoya and Sakaki 2013).

FTIR spectra of different acid pretreated biomass is given in Fig. 2. Typically, cellulose had strong IR absorbance of C–O (1050 cm^{-1}) stretching from C–OH and OH (3400–3200 cm^{-1}) existing in each unit and the absorbance of 2860–2970 cm^{-1} and 700–900 cm^{-1} were mainly attributed to C–H stretching. After orienting these in XRD patterns, it could be concluded that compared with raw biomass, absorbance of OH, C–OH and C–H in acid pretreated biomass were all stronger, responsible for the

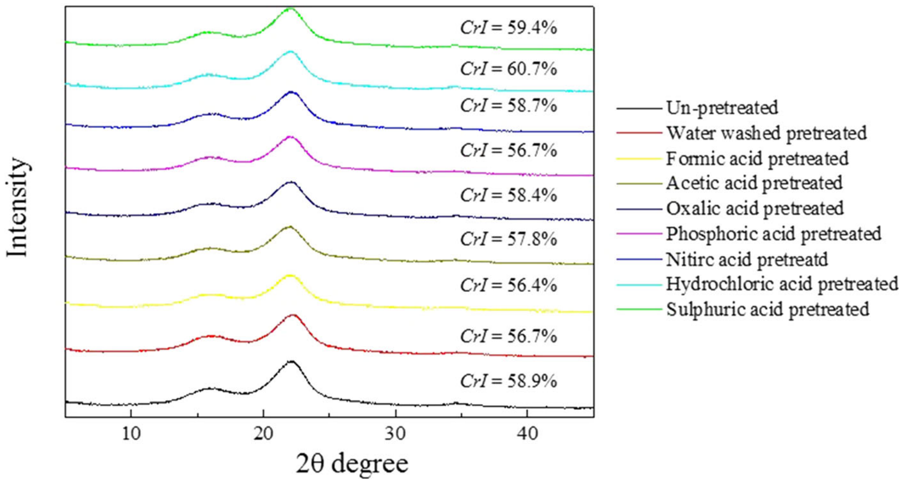

Fig. 1 XRD diffraction patterns of un-pretreated and pretreated biomass

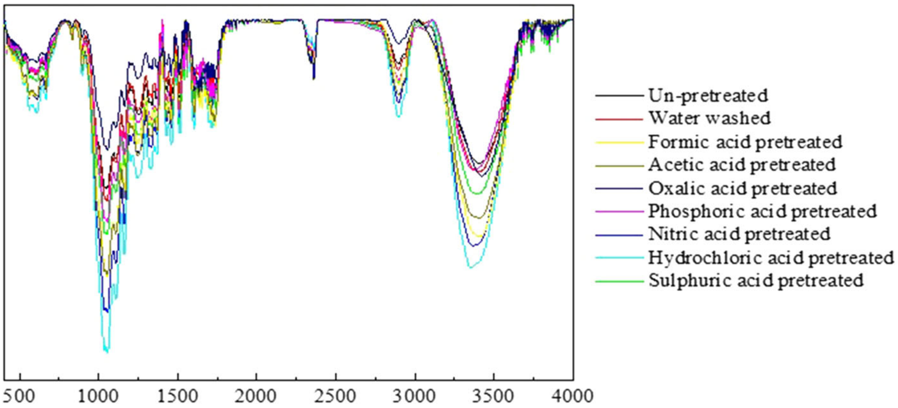

Fig. 2 FTIR spectra of un-pretreated and pretreated biomass

formation of levoglucosan where intermolecular dehydration originated from these activated groups. Moreover, biomass pretreated by hydrochloric acid obtained the strongest peaks.

Due to the differences on physical structure between raw materials and acid pretreated samples, in a pyrolysis process heat penetrates intensively on these solid central domains in acid pretreated biomass particles, significantly accelerating the reaction rate during thermal transition (Carpenter et al. 2014). Whereas, eased thermal stabilities in pretreated samples have no apparent effect on productions of monosaccharide's derivatives, which instead exhibits noticeable in the formation of char or gas yield considered translated from the lignin component (Bridgwater 2005). Hence, thermal parameters in this study were founded a performance relatively independent on the yields of levoglucosan or other fermentable productions obtained by fast pyrolysis, compared with the correlation between translation yields and the content of AAEMs. Moreover, a slight fluctuation was observed on the tested *CrI* as structural indexes in samples pretreated by different acids. Since there existing considerable changes in the content of AAEMs of raw and pretreated samples (decreased by up to 86.7%) while a limited alteration was tracked on *CrI* (increased by up to 3.1%), the impact of acid pretreatments at room temperature was implemented on AAEMs greater than biomass structures.

Thermal behavior of biomass

TG and DTG curves represent for the thermal weight loss are shown in Fig. 3, from which characteristic parameters of biomass thermal degradation are listed in Table 3. Two distinct peaks in biomass were presented in the DTG on account of the degradation of hemicellulose and followed by cellulose. Hemicellulose was decomposed easily, with the weight loss concentrated happened at 302.2–316.5 °C, soon afterwards cellulose pyrolysis was decomposed at a higher temperature ranging from 326.8 to 355.0 °C. For raw biomass, the initial devolatilization temperature (T_i)

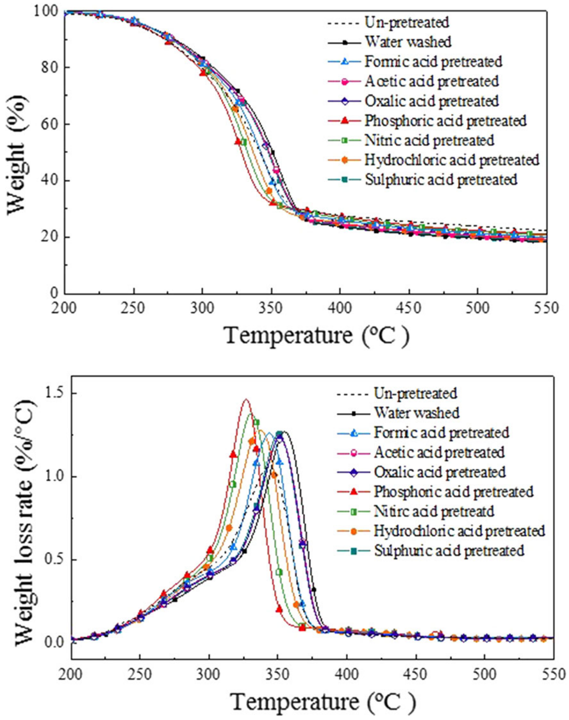

Fig. 3 TG and DTG curves of un-pretreated and pretreated biomass

Table 3 The pyrolytic parameters of biomass

Samples	T_i (°C)	T_t (°C)	T_{max1} (°C)	D_{max1} (%/°C)	T_{max2} (°C)	D_{max2} (%/°C)	M_r (%)
Un-pretreated	251.8	464.2	308.9	0.48	343.6	1.06	11.21
Water washed	258.0	382.2	316.5	0.46	355.0	1.27	5.85
Formic acid pretreated	258.5	416.5	310.5	0.46	343.9	1.26	7.31
Acetic acid pretreated	257.3	394.7	314.3	0.46	351.3	1.23	7.12
Oxalic acid pretreated	256.4	393.8	313.8	0.46	351.4	1.22	6.66
Phosphoric acid pretreated	253.7	436.2	302.2	0.47	326.8	1.46	7.03
Nitric acid pretreated	258.5	426.4	306.6	0.46	330.6	1.38	7.26
Hydrochloric acid pretreated	258.1	400.6	309.4	0.46	336.8	1.28	5.82
Sulphuric acid pretreated	256.3	386.0	314.0	0.45	350.5	1.25	6.38

T_i, pyrolysis initial temperature, pyrolysis temperature when the weight loss is 5%; T_t, pyrolysis end temperature, pyrolysis temperature at which the weight loss is 75%; T_{max1}, the temperature corresponding to the highest point of the first peak of DTG; D_{max1}, the weight loss rate corresponding to the highest point of the first peak of DTG; T_{max2}, the temperature corresponding to the highest point of the second peak of DTG; D_{max2}, the weight loss rate corresponding to the highest point of the second peak of DTG; M_r, final residue of pyrolysis

started at a lower temperature. The maximum DTG peak from cellulose pyrolysis also varied according to the value of $DTG_{\max}$, which represented the temperature of the maximum decomposition rate was achieved, and acid pretreated biomass had a relatively higher $DTG_{\max}$. Acid pretreatments at room temperature could increase the T_i and $DTG_{\max}$ by removing minerals and enhancing the thermal stability of biomass. In previous study, it was proved that Na^+, K^+ and Mg^{2+} could promote biomass degradation at low temperatures, so the thermal stability of biomass could be enhanced by removal of AAEMs (Le Brech et al. 2016). Furthermore, these involved thermal behaviors were considered with a noticeable interaction between metal trace in biomass, especially influenced by AAEMs. AAEMs affected the thermal degradation by catalyzing a series of reactions responsible for the formations of invaluable by-productions, performing as (1) a lower initial decomposition temperature, (2) a slower maximum degradation rate, (3) a decreased maximum degradation temperature, (4) an enhanced char and gas yields (Le Brech et al. 2016).

Fast pyrolysis of biomass

After enduring acid pretreatments, biomass was technically conveyed to fast pyrolysis. Yields of main compounds were analyzed (Table 4). According to the "Broido-Shafizadeh"—mode, the levoglucosan could be formed via biomass pyrolysis with two consecutive first-order reactions, the first step is the formation of "active cellulose", and then depolymerized by glycosidic bond scission into volatiles including levoglucosan or decomposed into char and gases (Ronsse et al. 2012). Besides, levoglucosan could be further decomposed light oxygenates, char and gases, as well as these representative oxygenates produced in levoglucosan decomposition such as 5-hydroxymethylfurfural, furfural and some C_1–C_2 compounds (Meng et al. 2016). The levoglucosan yield (0.3 wt%) was extremely low in the pyrolytic process of un-pretreated biomass, while it could be significantly enhanced after acid pretreatments. Regardless of acid types, productions of levoglucosan from the acids-pretreated biomass were considerably greater than that from raw biomass. Yields of levoglucosan from formic acid, acetic acid, oxalic acid, phosphoric acid, nitric acid, hydrochloric acid, sulphuric acid pretreated biomass were calculated as 14.3 wt%, 13.8 wt%, 12.5 wt%, 27.0 wt%, 23.1 wt%, 22.7 wt% and 22.0 wt%, respectively. In addition, the highest yield of levoglucosan (27.0 wt%) contributed from phosphoric acid pretreated biomass, precisely agreed with the result of total AAEMs that the phosphoric acid pretreated biomass contained the least content of AAEMs, where promotion on the generation of levoglucosan was maximized due to the most efficient

Table 4 Yields of main compounds from pyrolysis of biomass

Samples	Acetic acid[a]	Furfural[a]	n-Hexadecanoic acid[a]	Phenol[a]	Carbon dioxide[a]	Anhydro-D-galactosan[a]	Levoglucosan[b]
Un-pretreated	9.0	0.5	1.1	2.6	24.8	0.04	0.3
Water washed	5.7	0.05	0.7	2.2	11.3	0.1	11.6
Formic acid pretreated	4.4	0.06	0.6	1.0	5.6	0.7	14.3
Acetic acid pretreated	6.3	0.09	0.4	1.0	11.7	0.9	13.8
Oxalic acid pretreated	5.3	0.07	0.5	1.2	12.8	0.5	12.5
Phosphoric acid pretreated	1.4	0.08	0.4	0.7	6.6	0.7	27.0
Nitric acid pretreated	0.4	0.05	0.4	0.5	7.6	0.9	23.1
Hydrochloric acid pretreated	0.7	0.04	0.3	0.7	7.2	0.4	22.7
Sulphuric acid pretreated	2.6	0.05	0.5	0.8	10.7	0.4	22.0

[a] Relative content (%)

[b] Yield based on cellulose (wt%)

removal of AAEMs. There was an obvious tendency towards higher levoglucosan yields from sulphuric acid, nitric acid and hydrochloric acid pretreated biomass greater than those of formic acid, acetic acid and oxalic acid pretreated biomass, which negatively related to the evidence of total AAEMs content (Table 2) provided that less presentence of AAEMs could improve the levoglucosan yield. Besides, for phenolic compounds which derived from lignin in pyrolysis possessing an inhibition effect on subsequent bioconversion, sum of contents (0.5–1.2%) from acids pretreated biomass was lower than that from raw material (2.6%), as showed in Table 4. Thus, less content of phenol in pyrolysate achieved by acid pretreatments offered an unencumbered access to the subsequent bioconversion. From which, fast pyrolysis followed by acid pretreatments at an ordinary temperature was considered to have an enough capability to obtain a constituent substrate for fermentation, and the experimental results showed that biomass could be highly decomposed to levoglucosan by decreasing AAEMs, which could be utilized for wide implementation. In the previous works, biomass was pretreated by acid in serial concentrations ranged from 1 to 10 wt% at a high temperature (75 °C) and the distribution of pyrolytic products were quantified by a similar method (Jiang et al. 2017). Comparatively, acid pretreatments at room temperature produced considerable less furfural than that of similar pretreatment accompanied by heating. This could be explained by the production of furfural precursors under an un-mild temperature, known as the removal of hemicellulose content. Furthermore, biomass pretreated by acid at room temperature released a low content of carbon dioxide during fast pyrolysis, compared to that achieved by high-temperature pretreatment for an enhanced storage of CO_2 in rich-pored structure of biomass. Compared with acid pretreatments at high temperature, acid washing at room temperature could remove and passivate especially alkali metals from biomass prior to pyrolysis, and could significantly help in stabilizing levoglucosan after its formation during biomass pyrolysis. Thus, acid pretreatments at room temperature was concluded as a more profitable and commercial method to efficiently release the maximum fermentable sugars.

Conclusions

In this study, it was proved that acid pretreatments prior to pyrolysis could effectively accumulate levoglucosan production from biomass. Different acid pretreatments (formic acid, acetic acid, oxalic acid, nitric acid, phosphoric acid, sulphuric acid and hydrochloric acid) were employed at room temperature, and the pretreated biomass was rich in crystalline cellulose and poor in AAEMs, where the change in AAEMs was comparatively noticeable. Conclusively, the levoglucosan yield of H_3PO_4-pretreated biomass was remarkably improved to 27.0 wt% as compared with that of original material (0.3 wt%), which explained the practicability of acid pretreatments mildly. In conclusion, acid pretreatments at room temperature as a novel and economical strategy was proposed and researched, which could remarkably remove AAEMs and boost the wide implementation of this technology in the future.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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