



Isolation of Lignocelluloses via Acidification of Hydrolysates Induced from Different Straws

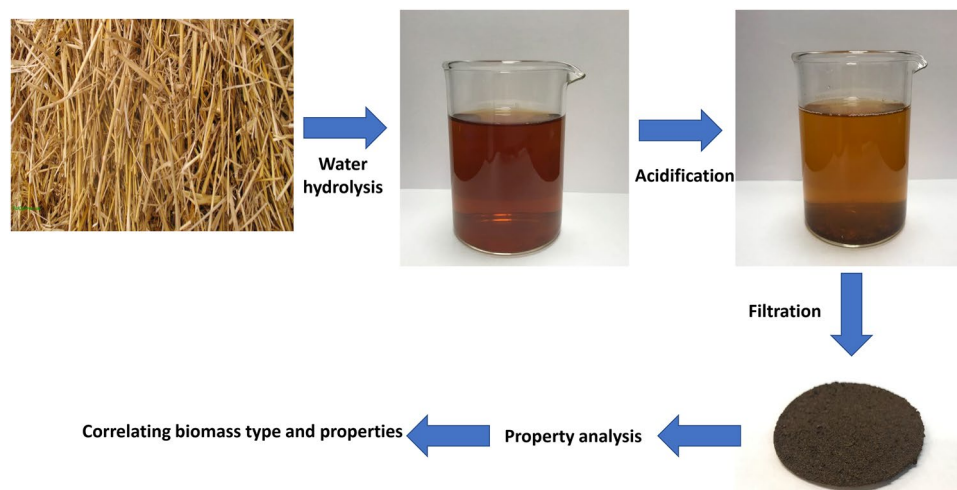
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Abstract

Hydrolysis has been commercially practiced for isolating hemicelluloses from wood chips. Acidification has also been reported as means to isolate lignocelluloses from hydrolysate. However, the performance of hydrolysis and subsequently acidification of induced hydrolysate on non-wood species is unclear. In this work, the hot water hydrolysis of wheat straw, rice straw and maize straw and the acidification of the generated hydrolysates were investigated. The hot water hydrolysis process of wheat, rice and maize straws were optimized. The effect of acidification on separating lignin from hydrolysates was also evaluated as a means to generate lignin. The properties of the collected lignocelluloses were determined to identify a potential application for them. The optimal conditions of the hydrolysis for straws were liquid/solid ratio of 12/1 (wt/wt), temperature of 170 °C and time of 60 min, which yielded rice straw hydrolysate containing more sugars than did the hydrolysates of wheat and maize straws. Acidification to pH 1.5 led to 27.49%, 29.17% and 23.38% lignin removals from the hydrolysates of wheat, rice and maize straws, respectively. Acidification decreased the furfural concentration of hydrolysates and increased the acetic acid concentration. The precipitates generated via acidification of hydrolysates had different heating values, thermal stability and ash content, and the precipitates of acidified rice straw hydrolysate had a higher heating value and thermal stability, but lower ash, than did those of acidified wheat and maize straws. The hot water hydrolysis of different straws could be conducted under the same conditions, but the acidification of hydrolysates would generate lignin with varied properties that may be suitable for altered applications. These results provide evidence for the impact of straw type on the thermal properties of extracted lignin of straw and thus its potential applications.

Graphic Abstract



Keywords Renewable materials · Lignocelluloses · Biorefining · Hydrolysis · Acidification

Extended author information available on the last page of the article

Statement of Novelty

Straws are available vastly in many countries, but they are currently wasted. In this work, lignin of straws was extracted via hot water hydrolysis of biomass and subsequently the acidification of generated hydrolysate. The results generated novel and concrete evidence that the hydrolysis and acidification could generally yield precipitates with different thermal properties, depending on the biomass resource, which would impact their potential valorization pathways.

Introduction

The excessive use of fossil fuels has caused serious pollution problems. It is necessary to decrease the use of fossil fuels by replacing them with bio-based fuels [1, 2]. An integrated forest biorefinery (IFBR) allows for the production of bio-energy and biomaterials, such as liquid fuel, ethanol, chemicals, and polymers in addition to traditional pulp and paper products [3]. It was estimated that 6.5×10^8 tons of wheat, rice and maize straws are produced as agricultural residues annually in China, but they are ineffectively utilized. As renewable materials, agricultural residues could be used to produce value-added products in biorefining systems [4].

Hydrolysis is a widely used method to extract hemicelluloses from lignocellulosic biomass [5–8], and the biomass after hydrolysis can be further used for pulping, for instance [9]. As a chemical-free and cost-effective process, hot water hydrolysis has attracted attentions [10–15]. In the hot water hydrolysis process, the hemicellulose of biomass is dissolved in the hydrolysate due to the catalytic action of acetic and other organic acids generated from the liberation of acetyl groups [10]. Some reports are available on the hydrolysis of straw. Hot water hydrolysis of the pelletized straw was conducted at the temperature of 170–210 °C for shorter than 40 min [1, 16, 17]. It was also reported that hot water hydrolysis of wheat straw at 200 °C for 30 min led to the isolation of 23.9 wt% of lignin and 49.2 wt% of C5 oligosugars [16]. The hydrolysis of rice straw with the particle size of 250–420 µm at 180 °C for 30 min led to 29.8 wt% of xylose isolation [17]. Another study reported that 90.5% xylan solubilization was achieved when corn stover with the size of 4.8 mm was pretreated at 210 °C for 10 min [1]. However, it is not clear if different straws could be hydrolyzed under similar hydrolysis conditions and if they induce hydrolysates with similar constituent concentrations. However, knowledge on this matter is important for developing biorefining systems that is flexible for utilizing different straws.

When produced, hydrolysate from hot water hydrolysis process contains hemicellulose, lignin, furfural and acetic

acid, and these chemicals require isolation for their potential use in valorized products [18, 19]. Altered approaches have been proposed for isolating lignin from hydrolysates, such as acidification by sulfuric acid [20], treatment with polyethylene oxide (PEO) or laccase [6, 21], adsorption by using activated carbon [22] and filtration by membrane [23]. Acidification is a commercial process for extracting kraft lignin from black liquor [24, 25] and was proved to be an effective approach for isolating lignin from hydrolysate of kraft-based dissolving pulp production process [26, 27]. Acidification can isolate lignin from hydrolysate facilitating the application of hydrolysate in producing value-added products. It was reported that the lignin of hydrolysate is a valuable raw material for producing bio-based polymers, such as polyurethanes and phenolic resin [27, 28]. Lignin could also be used as fuel [29]. However, it is not clear if acidification can be adapted for separating lignin dissolved in the hydrolysates of different straws. However, information on such an acidification process can help with the development of a biorefining process that utilizes different straw types and generate lignin as a product.

In this work, the hot water hydrolysis conditions of straws including wheat, rice and maize were optimized. The properties of the hydrolysates from hot water hydrolysis process were systematically investigated. Subsequently, the effect of acidification on the properties of hydrolysates, such as lignin, hemicellulose, furfural and acetic acid, were experimented, and the properties of the isolated materials were evaluated for proposing potential applications for them. One objective of this work was to optimize and evaluate the performance of hot water hydrolysis of different straws. Another objective of this work was to explore the impact of acidification of hydrolysates to isolate lignin for its potential use in the energy field.

Materials and Methods

Materials

The analytical grades of arabinose (99%), galactose (99%), glucose (99%), xylose (99%), mannose (99%), furfural (99%), acetic acid (99%) and sulfuric acid were purchased from Aldrich Company. Wheat straw, rice straw and maize straw were obtained from local farms located in the east of China and cut into 3–5 cm in length and washed thoroughly with cold water prior to use.

Biomass Analysis

Cellulose, hemicelluloses and lignin of straws were analyzed according to the NREL Laboratory Analytical Procedure of TP-510-42618. For lignin and sugar analysis, samples were

pretreated in a two-step acid hydrolysis: (1) primary hydrolysis of biomass in 72 wt% sulfuric acid at 30 °C for 1 h and (2) secondary hydrolysis of the hydrolyzed biomass in 4 wt% sulfuric acid at 121 °C for 1 h [30]. In the hydrolysis stage, cellulose and hemicellulose were converted into monosugars, which could be measured by Ion Chromatography (IC). The IC (ICS5000+, America Thermofisher) was equipped with CarboPacPA20 (3 mm × 150 mm) analysis column (CarboPacPA20, 3 mm × 30 mm) guard column and an electrochemical detector (ED), Au as the working electrode and Ag/AgCl as the reference electrode. Distilled water and 250 mM NaOH were the eluents at a flow rate of 0.4 mL/min. The column temperature was set at 30 °C. The concentration of acid insoluble lignin was measured using the combustion method at 575 °C for 24 h, while that of acid soluble lignin was measured by UV spectrophotometry at 205 nm. Ash content was tested according to TAPPI 211 0m-02. The chemical components (based on mass) of the straws were listed in Table 1.

Hot Water Hydrolysis of Biomass

The conditions of hot water hydrolysis of biomass were shown in Table 2. Temperature, liquid/solid mass ratio and time were optimized through the single factor experiment in the hydrolysis process. The hydrolysis process was carried out in a six-vessel rotating laboratory digester (Greenwood 2201-6, TX, USA). First, 20 g of straw (based on oven dried weight) and a certain mass of deionized water were placed and sealed in each pot of the digester. Then, the digester was heated to reach the set temperature at a heating rate of 2 °C/min and maintained for a certain time. After hydrolysis, the hydrolysates and solid were separated by a filter. Hydrolysis conditions were optimized for their highest sugar extraction from biomass. The sugar extraction yield was determined based on biomass's sugar content before and after the hydrolysis stage.

Acidification of Hydrolysate

To isolate lignocelluloses from hydrolysates, 50 mL of hydrolysates was acidified to different pH at room temperature by adding concentrated sulfuric acid (96 wt%), which agglomerated lignocelluloses and these agglomerated lignocelluloses were collected via centrifugation at 8000 rpm for 10 min and considered as precipitates. The acidified hydrolysate (at pH 1.5) and the precipitates after treatment were collected for further analysis (organic elements, thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC)).

Table 1 Chemical components of the straws (wt%)

Samples	Arabinose	Galactose	Glucose	Xylose	Lignin	Ash
Wheat straw	2.9 ± 0.1	0.6 ± 0.05	38.4 ± 0.2	29.6 ± 0.5	18.4 ± 0.2	4.5 ± 0.1
Rice straw	3.4 ± 0.2	1.4 ± 0.01	36.8 ± 0.3	25.2 ± 0.3	14.7 ± 0.2	7.5 ± 0.1
Maize straw	2.3 ± 0.1	0.7 ± 0.01	38.0 ± 0.2	26.4 ± 0.1	14.1 ± 0.1	4.6 ± 0.1

Table 2 The conditions of hot water hydrolysis

Temperature (°C)	Liquid/solid mass (wt/wt)	Time (min)
140, 150, 160, 170, 180	8/1, 12/1, 16/1, 20/1	40, 60, 80, 100, 120

Sugars and Lignin Analyses of Hydrolysate

The concentration of monosugars and oligosugars in the hydrolysate was measured by an ion chromatography (IC) (ICS5000+, America Thermofisher). The concentration of monosugars in the hydrolysate was determined by direct IC analysis of hydrolysate. For measuring the concentration of oligosugars, the hydrolysates were treated with 4 wt% sulfuric acid at 121 °C for 1 h in an oil bath for converting oligosugars to monosugars, as the IC can only detect monosugars [31]. The set-up conditions of IC were as stated previously. The total sugars of hydrolysates determined by monosugars and oligosugars of the hydrolysate.

The lignin content of hydrolysate was measured using a UV spectrophotometry at 205 nm according to TAPPI UM 250 [29]. Based on the concentrations of sugars and lignin in hydrolysates before and after acidification, the extraction yields of sugars and lignin from straw was determined following a mass balance.

Furfural and Acetic Acid Analysis of Hydrolysate

Furfural and acetic acid concentrations of hydrolysates were determined by using a high performance liquid chromatograph (HPLC) (LC-10ATvp SPD-10Avp, SHIMADZU) equipped with Waters C18 (4.6 × 150 mm, 5 μm) separation column. In this analysis, 0.1% H₃PO₄ was used as the eluent at a flow rate of 0.5 mL/min. The column temperature was set at 30 °C.

Element, Ash and High Heating Value Analyses

The organic elements of precipitates and hydrolysates were determined by using a Vario EL III Element Analyzer (Germany). The samples were first dried at 40 °C in a vacuum oven, and about 2–3 mg of the dried samples were transferred into the elemental analyzer. The samples were combusted at the high temperature of 1200 °C, and the carbon, hydrogen, oxygen, nitrogen and sulfur contents of the samples were determined based on the amounts of the generated gasses. The ash content of the hydrolysates was determined according to TAPPI T412.

The high heating values (HHV) of hydrolysates and precipitates were determined using Eq. (1) based on their elemental compositions and ash contents:

$$HHV = 0.3491C + 1.1783H - 0.1034O - 0.0211A + 0.1005S - 0.0151N \quad (1)$$

where C, H, O, A, S and N were the carbon, hydrogen, oxygen, ash content, sulfur and nitrogen contents (wt%) of the samples, respectively [32].

Thermogravimetric Analysis and Differential Scanning Calorimetric Analysis

The thermal stability of the precipitates was determined by using a thermogravimetric analyzer (TGA Q50, USA). The experiment was performed at a heating rate of 10 °C/min under nitrogen atmosphere. The samples were dried at 40 °C in a vacuum oven prior to analysis, and approximately 5 mg of dried samples were used in the TGA analysis between 0 and 800 °C. The DSC analysis of precipitates was conducted using a DSC Q20 instrument (USA). Approximately, 5 mg of dried samples was placed in aluminum pans and sealed in the sample pan press. The probes were heated from 0 to 400 °C at a rate of 10 °C/min under nitrogen atmosphere [33].

Results and Discussion

Optimization of Hot Water Hydrolysis Process

The objective of hydrolysis is to extract hemicelluloses from biomass [34]. Figure 1 shows the impact of process conditions of hot water hydrolysis on the sugar content of hydrolysate. It can be seen that the total extraction yield increased and then decreased with increasing temperature, time and liquid/solid ratio. The optimal conditions of hot water hydrolysis were liquid/solid ratio of 12/1 wt/wt, 170 °C and 60 min, in which extraction yield reached the maximum of 16.28%, 22.50% and 20.50% for wheat straw, rice straw and maize straw, respectively. The chemical components of hydrolysates are listed in Table 3. It can be seen from Fig. 1 and Table 3 that rice straw had more sugar, but less lignin and furfural in hydrolysate than did wheat straw and maize straw. It is well known that sugars can be degraded into furfural or other by products at a higher temperature than 170 °C and a duration of longer than 60 min [35].

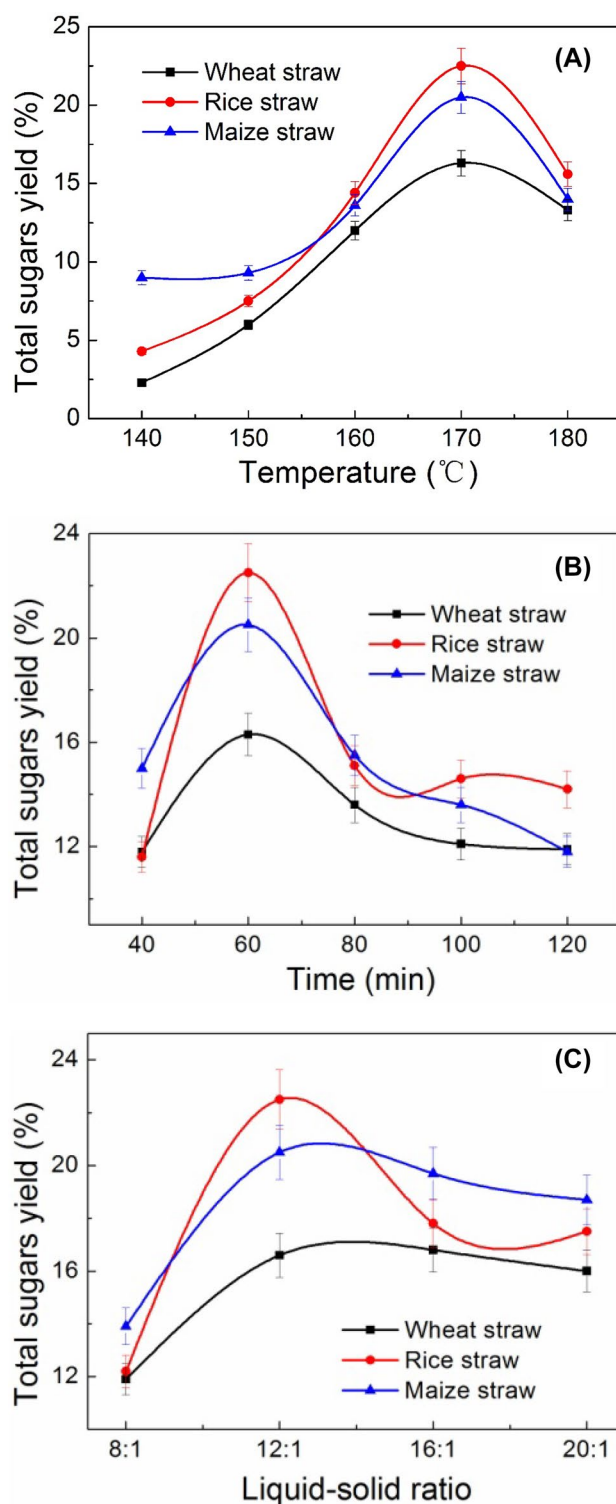


Fig. 1 Effects of (a) temperature (at liquid/solid mass ratio of 12/1, time of 60 min) (b) time (at 170 °C, liquid/solid mass ratio of 12/1) (c) liquid/solid ratio (at 170 °C and 60 min) on sugar content of hydrolysate

Table 3 Chemical components of hydrolysates at the optimal conditions of hot water hydrolysis

	Total sugars (g/L)	Monosugars (g/L)	Oligosugars (g/L)	Lignin (g/L)	Furfural (g/L)	Acetic acid (g/L)	pH value
Wheat straw	9.70 ± 0.2	0.99 ± 0.1	8.71 ± 0.1	4.24 ± 0.1	4.15 ± 0.1	2.28 ± 0.1	3.83 ± 0.2
Rice straw	12.52 ± 0.3	1.52 ± 0.1	11.00 ± 0.2	3.98 ± 0.1	2.38 ± 0.2	1.58 ± 0.1	4.30 ± 0.2
Maize straw	11.51 ± 0.2	2.50 ± 0.1	9.01 ± 0.1	5.05 ± 0.2	4.43 ± 0.1	1.47 ± 0.1	3.86 ± 0.2

Effect of Acidification pH on Sugars and Lignin of Hydrolysates

The objective of hydrolysis is to dissolve hemicelluloses in hydrolysate for producing value-added products. In the hydrolysis process, lignin with lower molecular weights would also dissolve, which could also hinder the subsequent utilization of hemicelluloses. Acidification is an effective approach to separate lignin from the hydrolysates. The effect of acidification pH on sugar and lignin removals (after centrifugation) is shown in Fig. 2.

It can be seen from Fig. 2 that total sugars and oligosugars of hydrolysates decreased after acidification, while the monosugars decreased first and then increased. The total sugar concentration of hydrolysates of wheat straw, rice straw and maize straw were 6.63, 9.12 and 8.76 g/L, respectively, which were reduced by 31.65%, 27.16% and 23.89%, respectively, when the hydrolysate was acidified to pH 1.5. Meanwhile, the oligosugars loss were 34.94%, 29.31% and 24.94%, respectively, which were higher than the total sugar loss. The reason is an increase in the monosugars content of the hydrolysate at pH 1.5. In addition, the lignin removal of hydrolysate of wheat straw, rice straw and maize straw were 27.49%, 29.17% and 23.38%, respectively, via acidification at pH 1.5. The hemicellulose and lignin contents of hydrolysate of hardwood decreased by 40% and 20%, respectively, via acidifying a pre-hydrolysis liquor produced industrially to pH of 1.5 [36], which implied that acidification could precipitate lignin and remove some hemicellulose from hydrolysates.

Effect of Acidification on Furfural and Acetic Acid of Hydrolysates

The furfural and acetic acid contents of hydrolysates before and after acidification is listed in Table 4. As seen from Table 4, acidification to pH 1.5 reduced the furfural concentration of hydrolysate of wheat straw, rice straw and maize straw (i.e., furfural removal of 32.8%, 24.8% and 18.7%, respectively). It was known that furfural could be degraded to formic acid with the addition of sulfuric acid to hydrolysate [37]. The acetic acid content of wheat straw, rice straw and maize straws increased by 14.5%, 7.0% and 12.3%, respectively, at acidification pH of 1.5. The reason for this increase might be the dissolution and conversion of

acetyl groups of hemicellulose into acetic acid under acute acidic conditions [38].

Effect of Acidification on the Elemental Compositions and Heating Values

The heating value of precipitates obtained through acidification of hydrolysate can be considered for evaluating lignin's potential as fuel. Table 5 lists the elemental compositions of original hydrolysates and precipitates after acidification at pH 1.5. Interestingly, the oxygen content of precipitates was lower than that of hydrolysates; while carbon, hydrogen (and hydrogen/carbon ratio) of the precipitates were higher. The nitrogen content of hydrolysate and precipitates were similar, but precipitates had more sulfur content, which was attributed to the presence of H₂SO₄ in the acidified hydrolysates. The precipitates of wheat straw had higher ash content than other straws. Heating values, elemental components and ash content of hydrolysates and precipitates were shown in Table 5. It is seen in Table 5 that the precipitates had higher heating values than did hydrolysates. The precipitates of rice straw showed the highest heating values of 20.90 MJ/kg. However, the heating value of precipitates of hardwood was reported to be 21.61 MJ/kg [36].

It can be seen in Table 5 that the hydrolysate of maize straw had a higher ash content than did wheat straw and rice straw, which was due to the fact that wheat straw and rice straw had a higher SiO₂ content than did maize straw [39]. SiO₂ was reported to be stable and remained in the wheat straw and rice straw after hot water hydrolysis, while only a part of its inorganic salt can be dissolved in hydrolysates [40].

Thermal Gravimetric Analyzer (TGA) Analysis of Precipitates

The TGA and DTG analysis of the precipitates from acidification are shown in Fig. 3. It can be seen from Fig. 3 that the degradation of precipitates occurred in a wide temperature range (100–800 °C). The pyrolysis patterns of precipitates of wheat straw and rice straw were similar when the temperature was below 600 °C. The weight loss in the range of 100–150 °C was probably due to the evaporation of moisture and other volatile components (e.g., furfural and acetic acid). Hemicelluloses would be decomposed in the temperature

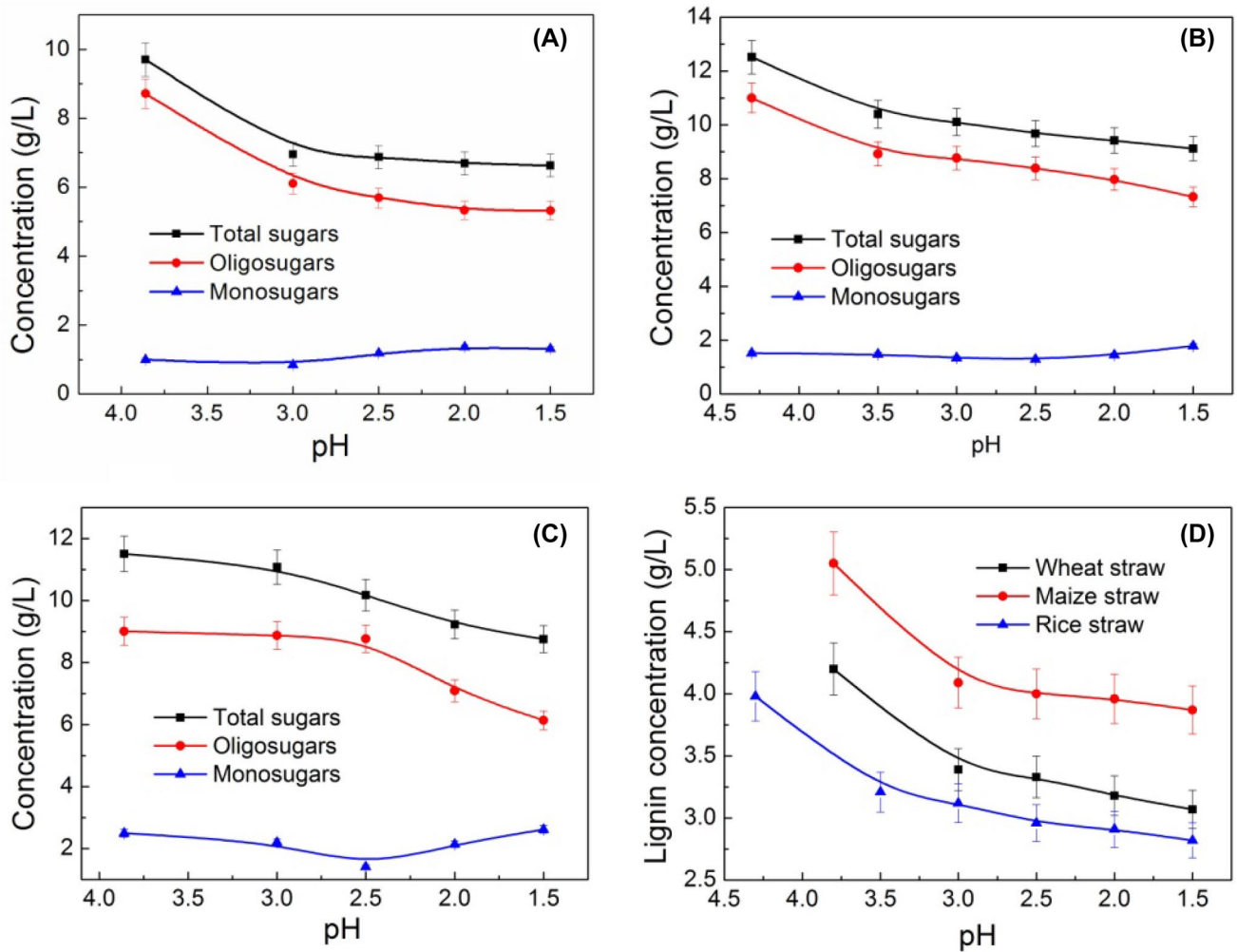


Fig. 2 Effect of acidification pH on sugars concentration of hydrolysates of (a) wheat straw (b) rice straw (c) maize straw and on the lignin concentration of hydrolysates (d) (The pH of original hydrolysates of wheat straw, rice straw and maize straw were 3.83, 4.30 and 3.86, respectively)

Table 4 Concentration of furfural and acetic acid in the original and the acidified (pH 1.5) hydrolysates

	Wheat straw		Rice straw		Maize straw	
	Hydrolysate	Acidified hydrolysate	Hydrolysate	Acidified hydrolysate	Hydrolysate	Acidified hydrolysate
Furfural (g/L)	4.15 ± 0.1	2.79 ± 0.2	2.38 ± 0.2	1.79 ± 0.1	4.43 ± 0.1	3.60 ± 0.2
Acetic acid (g/L)	2.28 ± 0.1	2.61 ± 0.3	1.58 ± 0.1	1.69 ± 0.1	1.47 ± 0.1	1.65 ± 0.3

Table 5 Elemental analysis (based on dry) of original hydrolysates and precipitates made from acidification (pH 1.5) of hydrolysates

	Wheat straw		Rice straw		Maize straw	
	Hydrolysate	Precipitates	Hydrolysate	Precipitates	Hydrolysate	Precipitates
C (wt%)	41.89 ± 1.3	43.07 ± 0.8	42.86 ± 1.6	45.93 ± 1.9	39.90 ± 0.9	47.75 ± 2.0
H (wt%)	5.40 ± 0.5	8.54 ± 0.7	4.46 ± 0.2	7.71 ± 0.4	1.76 ± 0.1	5.88 ± 0.8
O (wt%)	49.79 ± 1.3	43.20 ± 0.1	51.37 ± 1.3	41.14 ± 1.0	54.92 ± 1.2	42.41 ± 0.7
S (wt%)	0.12 ± 0.02	2.47 ± 0.1	0.08 ± 0.02	1.78 ± 0.2	0.09 ± 0.01	0.48 ± 0.04
N (wt%)	0.809 ± 0.1	0.812 ± 0.1	1.235 ± 0.2	1.447 ± 0.1	1.329 ± 0.2	1.467 ± 0.2
Ash (wt %)	6.58 ± 0.3	10.86 ± 0.2	7.82 ± 0.4	5.45 ± 0.1	12.64 ± 0.3	11.62 ± 0.2
HHV (MJ/kg)	15.70 ± 0.9	20.64 ± 0.4	14.73 ± 0.6	20.90 ± 1.0	10.05 ± 0.3	18.99 ± 1.5

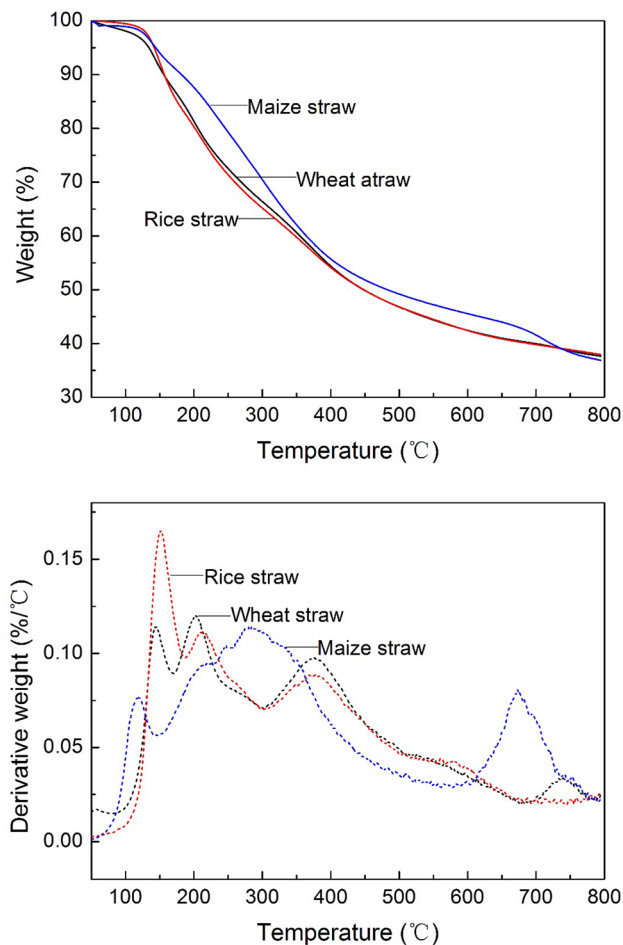


Fig. 3 Weight and weight derivative of precipitates from hydrolysates acidification process at pH of 1.5

range of 170–300 °C, while lignin would decompose in the temperature range of 200–500 °C in the pyrolysis process [41]. The weight loss in the range of 600–800 °C was probably related to the decomposition of inorganic alkali metal compounds of ash [42]. The precipitates of maize straw and wheat straw had an obvious weight loss peak in the range of 600–800 °C, while the precipitates of rice straw had a small weight loss peak at 600 °C, which was in accordance with the lowest ash content of precipitates of rice straw, and the highest ash content of precipitates of maize straw (Table 5). The residual quantity (i.e., char) of precipitates was about 37% after pyrolysis. It was reported that the residual quantity of kraft lignin separated from black liquor via acidification (pH lower than 3) was about 40% [43].

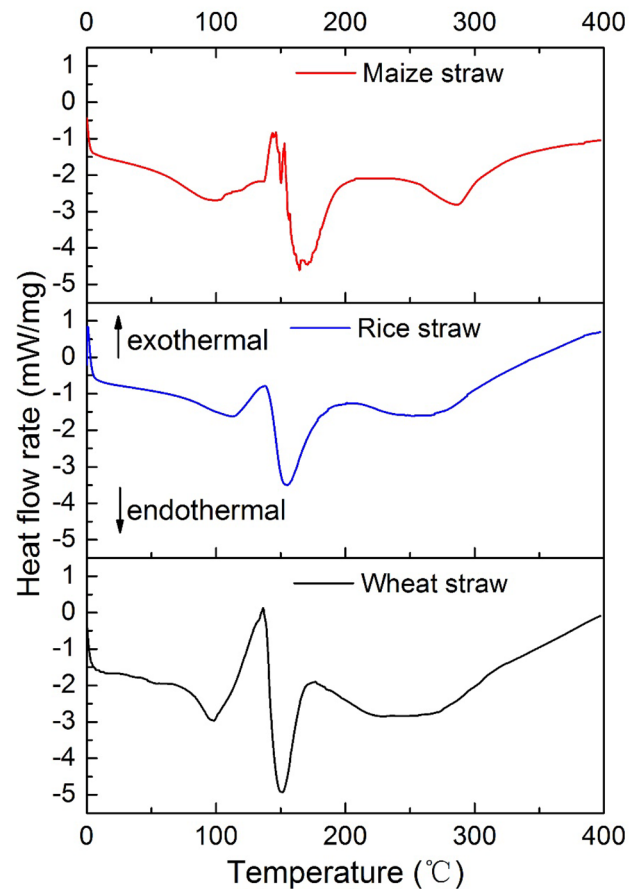


Fig. 4 DSC curves of precipitates made from acidification of hydrolysates

Differential Scanning Calorimetry (DSC) Analysis of Precipitates

DSC analysis is sensitive to slight compositional changes and shows energy consumption as a matter of changes in the state of material [33, 41]. The results of DSC analysis are shown in Fig. 4. Due to the moisture removal, the DSC analysis showed an endothermic peak around 100 °C [41]. When the temperature increased further, the DSC curves of precipitates showed a significant exothermic peak at 130–140 °C and a large endothermic peak at 150–170 °C. Polymerization of lignin or sugars may occur in the temperature range of 130–140 °C, which would contribute to an increase in the molecular weight of the precipitates. This exothermic behavior may be due to the polymerization, while the endothermic behavior in the temperature range of 150–170 °C may be due to the removal of side chain or the depolymerization of polymer chains [44, 45]. Further increasing the temperature led to the exothermic behavior (i.e., the decomposition) of biomass. In addition, the

precipitates of rice straw exhibited the smallest exothermic and endothermic peaks when the temperature was lower than 200 °C.

Conclusions

In hot water hydrolysis process of wheat straw, rice straw and maize straw, the optimal conditions were 170 °C, 60 min and liquid/solid ratio of 12/1, and the hydrolysate of rice straw had more sugars than that of wheat and maize straws. Acidification (at pH of 1.5) resulted in the lignin removal of 27.49%, 29.17% and 23.38% from the hydrolysates of wheat, rice and maize straws, respectively. In addition, the furfural concentration of hydrolysates decreased while acetic acid concentration increased after acidification. The heating value, thermal stability and ash of the lignin precipitates from acidification process were different for these straws. The precipitates of acidified rice straw hydrolysate showed a higher heating value, higher thermal stability and lower ash than those of acidified hydrolysates of wheat and maize straws. Thermal properties of precipitates from acidification process depended on the straw species.

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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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