

# A Continuous Hydrothermal Saccharification Approach of Rape Straw Using Dilute Sulfuric Acid

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**Abstract** The fossil fuel crisis in the world has raised much concern on developing biomass energy. Fermentable sugars are an important product which can be converted to bioethanol. Although sulfuric acid saccharification is a good method for breaking lignocellulose biomass, efficiency is not well-promoted in dilute acid, as many fermentation inhibitors are co-produced. A continuous saccharification approach was established in this study to reach high saccharification efficiency and low toxicity of reducing sugar (RS). The dilute  $\text{H}_2\text{SO}_4$  was taken as flow phase in this process with temperature gradient elevation. Each sample of 250 ml was taken when temperature elevated from 60 to 230 °C (temperature interval 20–30 °C). Under optimum conditions, the maximum RS yield ratio reaches 53.4 %. Furfural is detected in the hydrolysate, with a concentration less than 1.06 g/l. The optimized saccharification conditions were achieved at a flow rate of 25 ml/min and with  $\text{H}_2\text{SO}_4$  concentration at 1.0 %. Operation parameters were investigated including acid flow rate and acid concentration. The composition of rape straw is analyzed, and the material balance is studied in the optimized conditions. In addition to SEM, FT-IR analysis techniques are used, and the results show that the hemicellulose and cellulose in the rape straw can be fully converted to RS, while the change in lignin amount is negligible. This method is a novel and promising technique for high yield of RS, as it is accompanied with a low content of bio-inhibitor.

**Keywords** Hydrothermal saccharification · Rape straw · Dilute sulfuric acid · Reducing sugar

## Introduction

The world economy could not grow without energy supply, especially petroleum resources. However, with the increase in world population, more and more energy is required for social industry development. A survey reveals that current energy consumption is 16 times higher than the end of last century. Among them, the petroleum energy proportion is over 85 %. It is predicted that the existing oil reserves in the world can be exploited for only another 52.9 years for human beings [1, 2]. Therefore, the fossil energy is depleting and the world is facing serious a fossil energy crisis, which raises more international interest in developing biomass energy [3].

Bioethanol, as a sustainable promising alternative to fossil fuel, has many advantages both in reducing the emission of greenhouse gases and in alleviating other environmental problems [4]. In consequence, many scientists focus on the second-generation bioethanol product which is converted from agricultural residues, typically lignocellulose and cellulose biomass [5]. China has abundant agricultural residue resources, such as rape straw and wheat straw. Generally, the process of producing ethanol from biomass can be divided into the following three stages [6–9]. Firstly, the lignocellulose biomass is pretreated, which makes it easy to be hydrolyzed. Secondly, the pretreated biomass is hydrolyzed by acid or enzymatic method to obtain fermentable sugars, such as reducing sugar (RS). Thirdly, the sugar is fermented by yeast to produce ethanol. In these stages, a conversion from biomass to RS is a key process for efficient biomass utilization. Recently, numerous methods have been developed for the hydrolysis of cellulose with enzymes, acid, and supercritical

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water [10–13]. Among these methods, enzymatic and acid hydrolysis methods are effective. As for enzymatic method, better stability of RS can be obtained with high efficiency. However, it requires a long reaction time and thorough pre-treatment, is difficult to separate, and has high cost, which makes it hard to apply [3, 14]. Another method, i.e., solid acid catalyst, has been studied for its advantages of separation [15–17]; however, hot water in the reactor is detrimental to many solid acids, leading to the loss of its surface area and active sites. These shortages should be overcome before application [9]. Lastly, the dilute acid method can solve neutralization and corrosion problems [18]. Usually, it needs extreme conditions of high temperature and pressure [19–21]. The acid hydrolysis reaction rate is relatively high, but the low yield rate and fermentation inhibitor generation should be noticed. It has been reported that 1.0 % (w/w) H<sub>2</sub>SO<sub>4</sub> may be used as a catalyst at the high pressure of 42.0 MPa and temperature of 493 K [22, 23]. It has a high hydrolysis rate with a short retention time. Some monosaccharides are significantly degraded to fermentation inhibitors, e.g., acetic acid, furfural, hydroxylbenzaldehyde (HBA), 5-hydroxymethyl furfural (HMF), levulinic acid, siringaldedyde (SGA), and vanillin [24–27].

Therefore, it is imperative to develop a novel hydrolysis process which can obtain much sugar and few toxic compounds. A hydrothermal saccharification approach using continuous dilute H<sub>2</sub>SO<sub>4</sub> is established in this study. The reaction temperature ranges from 60 to 230 °C, and the acid concentration ranges from 0 to 1.0 % (w/w). Significantly, the hydrolysis reaction mechanism is also studied. This research is valuable for utilizing farm residues effectively.

**Materials and Methods**

**Raw Materials**

The rape straw samples, with a chemical composition detailed in Table 1, were collected from a farm at Nanhui town, Shanghai, China. They were cut into pieces of 1–2 cm after air-dried. The dried samples were ground and sieved to a size of 380–420 μm.

**Operation**

The continuous saccharification equipment was designed for the hydrolysis of rape straw. The process flow diagram of this system is shown in Fig. 1. It consists of feeding unit, reactor body, and sample collector. The feeding unit is made up of dilute acid tank, feeding pump and pipeline. The reactor body is a 250 ml autoclave coupled with magnetic force stirrer. It worked at a temperature range of 60–230 °C at 2 Mpa and at the stirring speed range of 100–150 r/min. The last unit is the

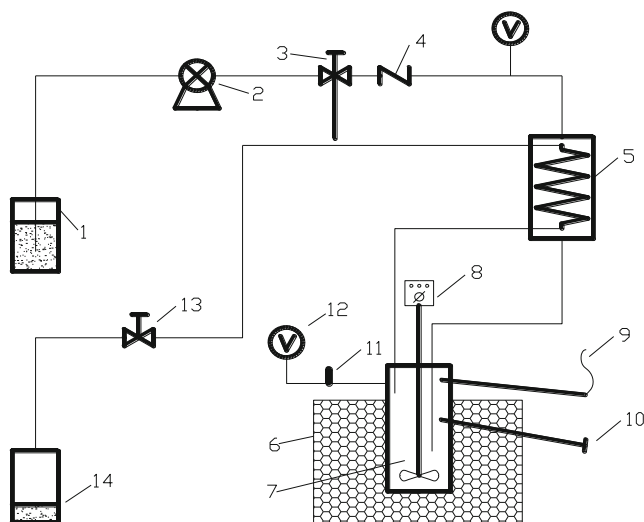
**Table 1** The chemical composition of rape straw

Composition	Proportion
Cellulose	49.52 %
Hemicellulose	12.69 %
Lignin	17.72 %
Moisture	9.70 %
Ash	6.54 %
Others	3.83 %

sample collector, which consists of sampling pipe and collection tank. To make full use of heat energy, the inlet and outlet go through a heat exchanger.

To make the reaction continuous, a high-pressure plunger pump was used in the system. First, the dried sample of rape straw was placed in the autoclave. Next, the dilute acid was pumped into the reactor. The pressure gauge of reactor was monitored for any increase in pressure; once this was observed, it indicated that the reactor was full of dilute H<sub>2</sub>SO<sub>4</sub>. The pump was stopped and the inlet valve was closed. After that, the heating procedure was started to increase the temperature.

The volume of inlet and outlet needed to be maintained. In the first stage, the temperature was set at 60 °C, and the dilute acid was pumped into the reactor. Sugar liquid was collected from the outlet once the pressure reached above 2 Mpa. In the second stage, sampling was maintained when the temperature at 90 °C. After the sampling process was finished, the hydrolysis reaction turned to the next stage. Sampling occurred at the temperatures of 110 °C, 130 °C, 150 °C, 170 °C, 190 °C, 215 °C, and 230 °C respectively.



**Fig. 1** The process flow diagram of continuous hydrothermal saccharification system. 1—dilute acid tank; 2—high-pressure plunger pump; 3—inlet valve; 4—check valve; 5—heat exchanger; 6—heater; 7—stirring rod; 8—control panel; 9—thermo (electric) element; 10—autoclave body; 11—relief valve; 12—pressure gauge; 13—discharge valve; 14—sample collection tank

The acid flow rate and acid concentration are the most important factors related to saccharification efficiency. In this study, 24.0 g rape straw was taken as the research subject, with a flow rate of 6, 10, 15, 20, and 25 ml/min; H<sub>2</sub>SO<sub>4</sub> (0.1 % w/w) solution were applied to hydrolyze the reaction. Dilute H<sub>2</sub>SO<sub>4</sub> concentrations of 0, 0.05, 0.1, 0.5, and 1.0 % were used to hydrolyze rape straw. Finally, the optimized flow rate and dilute H<sub>2</sub>SO<sub>4</sub> concentration were selected. The subsequent analysis process was carried out on the basis of the optimum conditions.

## Analytical Methods

### Composition Analysis

The content of neutral dietary fibre (NDF), acid detergent fibre (ADF), lignin, and cellulose were determined using the detergent method according to Van Soest [28, 29]. Hemicellulose content was calculated from the difference between NDF and ADF. Moisture and ash was determined by weight loss and dry ash methods.

### RS Analysis

RS was estimated by the DNS method [30]. Firstly, 1 ml filtered reaction solution was transferred to a conical flask (10 ml) and made up with distilled water. Then 1 ml diluted liquid was placed in a colorimetric tube (25 ml), followed by adding 1 ml DNS reagent. The mixture was boiled for 5 min in the water bath reactor, cooled to room temperature, and distilled water added up to the mark. Absorbance values of samples were taken at 540 nm in a UV–Vis spectrophotometer 1600 (Mapada Instrument Co., Ltd.). The RS yield rate is calculated by the equation below.

$$RS\ yield\ (\%) = \frac{\text{total mass of RS (g)}}{\text{total mass of rape straw (g)}} \times 100$$

### Furfural Analysis

UV spectrophotometry method was used to determine the content of furfural in the hydrolysate. Furfural concentrations of 0.50, 1.00, 2.00, 4.00, and 10.00 mg/l were configured by full wavelength scan. The maximum ultraviolet absorption spectrum of furfural is 276 nm. The standard curve was established in the range of 0.50–10.00 mg/l with the following equation,

$$Y = 0.1162 + 0.15913X$$

where X is the absorbance values of furfural, Y is the furfural concentration (mg/l). The correlation coefficient is

0.9992. The content of furfural in the hydrolysate was determined by this method according to the above equation.

### SEM Analysis

The scanning electron microscopy JSM-7401F (FE-SEM, JEOL, Japan) was used for observing the microstructure of native rape straw. Residues were collected at different stages and analyzed by the same method. The microscope was operated at a voltage of 20 kV.

### GC-MS Analysis

To analyze the by-product generated in thermal hydrolysate, GC-MS analysis were performed using a GCMS-QP2010 apparatus (SHIMADZU, JP, Ltd), equipped with DB-5 MS column (30 m×0.32 mm, 0.25 μm film thickness). The chromatographic conditions were as follows: a carrier gas (He) flow rate of 50 cm/s, initial temperature of 40 °C for 5 min, temperature of 10 °C/min for 30 min, injector and transfer-line temperature of 250 °C. The split ratio is 1:10. MS detects at: voltage 1.01 KV, EI 70 eV, scan field 29–350 m/z, ion source temperature (200 °C).

### FT-IR Analysis

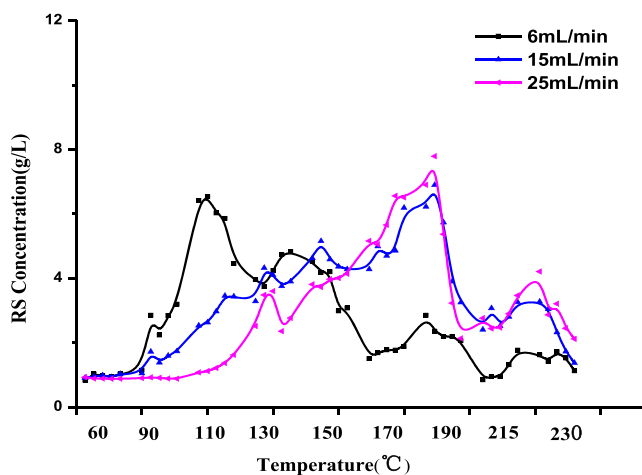
Fourier transform Infrared (FT-IR-21) spectroscopic analysis was used to detect the change of functional groups caused by dilute acid hydrolysis under various temperature conditions. FT-IR spectrum was recorded between 4,000 and 5,000 cm<sup>-1</sup> using a Shimadzu Spectrometer with detector at 4 cm<sup>-1</sup> resolution and 25 scans per sample. Disks were prepared by mixing 3 mg of dried sample with 300 mg KBr (spectroscopic grade) in an agate mortar. The resulting mixture was pressed at 10 MPa for 3 min.

## Results and Discussion

### RS Yield and Optimized Conditions

#### *The Effect of Sulfuric Acid Flow Rate on RS Yield*

Figure 2 shows various RS concentration at different flow rates. At the flow rate of 6 ml/min, RS yield reaches the maximum of 6.54 g/L at 110 °C, then it decreases slowly. The total RS content is 6.02 g. The concentration peak of RS appears earlier than other flow rates (15, 20 ml/min). At the flow rate of 15 ml/min, the concentration of RS achieves its highest peak value of 6.89 g/L at 180 °C, then it decreases dramatically. In this condition, total RS is gained almost the same amount with that at 6 ml/min. At a flow rate of 25 ml/min, the peak value of 7.79 g/l is achieved at 180 °C. The total



**Fig. 2** Effect of flow rate on RS concentration of rape straw

RS is 6.65 g, similar to those of the former two (6.15 ml/min). It is quite clear that the peak of RS concentration appears earlier at a low flow rate. When the flow rate is low, the retention time is long; the hydrolysis reaction will be completed, as shown by the appearance of a low flow rate (6 ml/min). A high flow rate makes the product separate in a timely fashion. After the peak, the RS concentration decreases gradually. This is mainly due to the exhaustion of cellulose and hemicellulose content. Meanwhile, RS decomposes at high temperature.

At a high flow rate, high saccharification efficiency can be achieved as RS yield ratio of raw rape straw is quite high. The fermentation cannot occur at this stage (temperature below 110 °C), as the RS concentration is quite low. They should be collected separately. The highest sugar concentration in the solution is almost high enough for fermentation directly. The total volume of solution can be kept almost the same by shortening the collection time. So a flow rate of 25 ml/min is suitable for the hydrolysis of rape straw in subsequent experiments.

#### *The Effect of Sulfuric Acid Concentration on RS Yield*

Evidently, it is shown from Fig. 3 that increasing acid concentration will dramatically increase the concentration of RS, as well as its total mass. Without H<sub>2</sub>SO<sub>4</sub>, only a low RS concentration peak appeared. Over the course of the reaction, the concentration of RS slightly increases till the highest peak. The maximum concentration is about 5.84 g/l. Then it decreases to a very low level. About 4.0 g RS is collected under this condition. The trend of 0.05 % (w/w) H<sub>2</sub>SO<sub>4</sub> is similar to that without H<sub>2</sub>SO<sub>4</sub>. The RS peak value is about 5.77 g/l. A total RS of 4.0 g is obtained. When the H<sub>2</sub>SO<sub>4</sub> concentration is 0.1 % (w/w), the RS concentration variation trend is similar to the former two (0, 0.05 %). The peak value of 7.79 g/l is achieved at 180 °C. Then it decreases to a low level. The total

RS is about 6.65 g. As H<sub>2</sub>SO<sub>4</sub> concentration increases to 0.5 % (w/w), RS peak concentration value is about 9.87 g/l. The total RS content is 10.11 g in this process. The concentration of RS increases rapidly with the increase of the acid concentration. A noticeable shift in sugar concentration is evident when H<sub>2</sub>SO<sub>4</sub> concentration is 1.0 % (w/w). The reaction quickly increases to its maximum concentration of 20.06 g/l. Then it decreases rapidly to a low level. This is mainly due to the effect of acid concentration. Yang [31] has studied the effect of H<sub>2</sub>SO<sub>4</sub> (in a range of 0–1.0 mol/l) concentration on the yield of glucose, xylose in the first stage hydrolysis of cotton straw. The sugar yield is rapidly increased with the rise of acid concentration. Similarly, the effect of acid concentration on total sugar yield of lignocellulose biomass was investigated by Lenihan [20]. Increasing the acid concentration is a more effective way to maximize sugar yield than increasing the temperature. Actually, both the higher concentration of acid and temperature lead to higher sugar yield. High temperature leads to high activity of H<sup>+</sup> ions with the same H<sup>+</sup> concentration. As for low-concentration acid, it could not supply enough of H<sup>+</sup> ions to hydrolyze rape straw completely. However, at during the high temperature period, a relatively high activity of H<sup>+</sup> ion is provided to hydrolyze rape straw. As for 0.05 %, 0.1 %, and 0.5 % H<sub>2</sub>SO<sub>4</sub>, the peaks of RS concentration appeared at the end of the high temperature period, 160–170 °C. As for 1.0 % H<sub>2</sub>SO<sub>4</sub>, the RS peak was achieved below 110 °C.

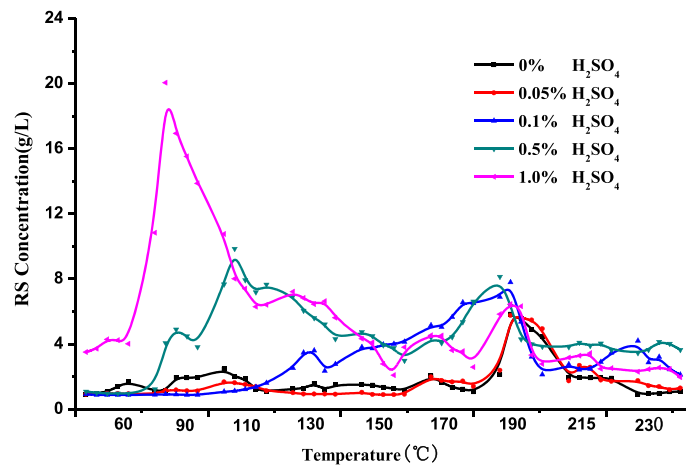
In optimum condition, 12.81 g RS is collected in the hydrolysis process. The RS yield rate reaches 53.4 %, which is 38 % higher than that of 0.05 % dilute acid. From Fig. 3 it can be concluded that the acid concentration has an important relationship with the total content of RS. The RS yield rate rises rapidly with the increase of acid concentration. This point is also consistent with the studies of Hernández et al. [32].

#### *Furfural Generation Under Optimized Conditions*

From Fig. 4, furfural concentration increases as the temperature increases; the maximum concentration is at 130 °C, after which it shows a decreasing trend. At a temperature range of 60–130 °C, furfural concentration increases quickly until the highest furfural concentration (1.06 g/l) is achieved. When the temperature was in a range of between 150 and 215 °C, furfural concentration decreased to a medium level between 0.4 and 0.7 g/l. As the temperature increases to 230 °C, furfural concentration goes below 0.1 g/l.

Compared to the RS concentration in the whole process, the maximum concentration of RS occurred before furfural maximum concentration. Furfural concentration is below 0.40 g/l when the highest RS concentration reaches 20.07 g/l. This is ideal for the separation of RS and furfural from hydrolysate. The RS is in medium concentration (7.0 g/l)

**Fig. 3** Effect of sulfuric acid concentration on RS concentration of rape straw



when furfural reaches its maximum value. This may result from the decomposition of related sugars, such as pentose and xylose. In short, the RS concentration is much higher than that of furfural. Furfural concentration is below 1.06 g/l, which is much lower than the batch method used in our previous research.

### The Characterization of Rape Straw

#### SEM Analysis

The residues at each stage with different temperatures are scanned by SEM. Initially, the native sample of rape straw appears a rigid surface which demonstrates a laminated and branched structure (Fig. 5a). The residue of 60 °C still exhibits a similar structure to the native one (Fig. 5b). The residue of 90 °C shows some holes on its surface, which means the original structure is leaving its original shape (Fig. 5c). This morphology is generally kept till 150 °C (Fig. 5d, e, f). As

seen in Fig. 5g, the residue of 170 °C becomes smaller than the former samples. Many porous shapes appear on the surface of the residue, shown in Fig. 5h. The residue of 215 °C shows highly corroded dots. A distinct decomposition occurs at this stage (Fig. 5i). The last sample of 230 °C exhibits many crushed particles (Fig. 5j). At high temperature, the rigid surface structure has been broken down. The fiber skeleton begins to be ruptured above 150 °C. It indicates that the saccharification process is completed below 150 °C.

To conclude, the surface morphology of rape straw residues shows that the untreated sample has a smooth surface structure. With the increase of temperature, particle size reduces and the matrix disrupts. The surface becomes rough, and there is evidence of multiple pores.

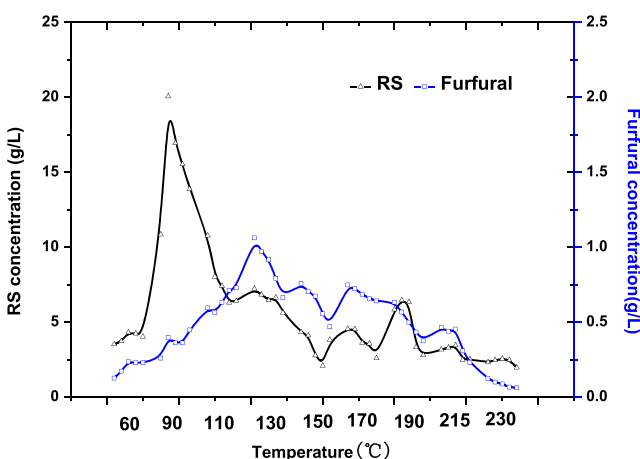
#### GC-MS Analysis

In order to know the generation of by-products, the hydrolysate under optimized conditions is analyzed by GC-MS. The result is shown in Fig. 6.

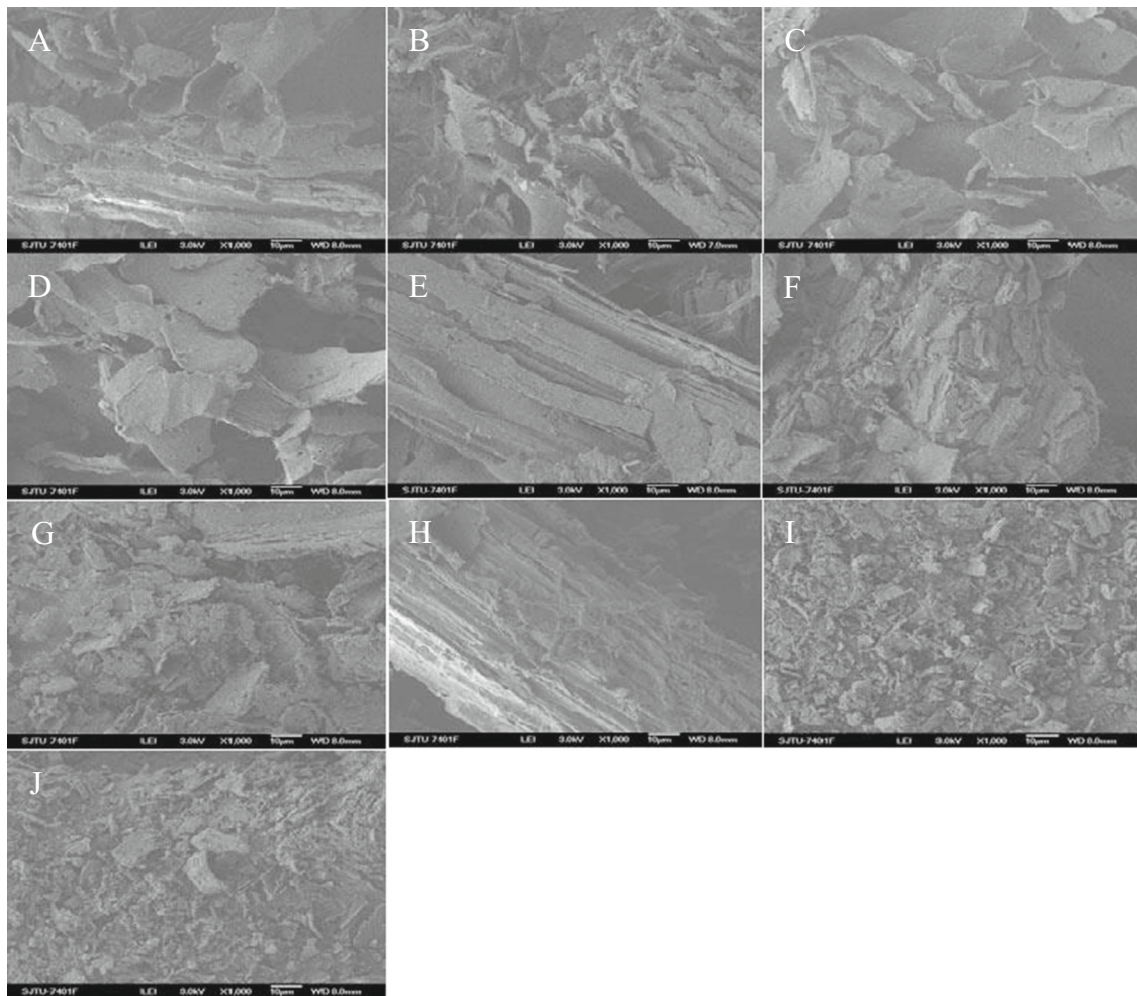
In 1.0 % H<sub>2</sub>SO<sub>4</sub> continuous solution at 110 °C, furfural is the only identified by-product, with a ratio of 89.24 % in the hydrolysate, and other compounds are about 10.76 %, as shown in Table 2. The reasons have been explained below.

Firstly, as xylose is degraded rapidly to furfural during acid hydrolysis, furfural is usually detected in the hydrolysate of biomass. In the research of Herrera [33], the maximum concentration of xylose was obtained in 2 % HCl solution at 100 °C. Furfural was produced due to undesired secondary reactions of xylose at temperature higher than 100 °C. As xylose is separated in a timely manner from the reactor during the high-temperature period, its generation rate must be greatly reduced.

Additionally, degradation products of RS, such as 5-hydroxymethyl furfural (HMF), hydroxybenzaldehyde (HBA), or siringaldeddyde (SGA) [27] are not determined.

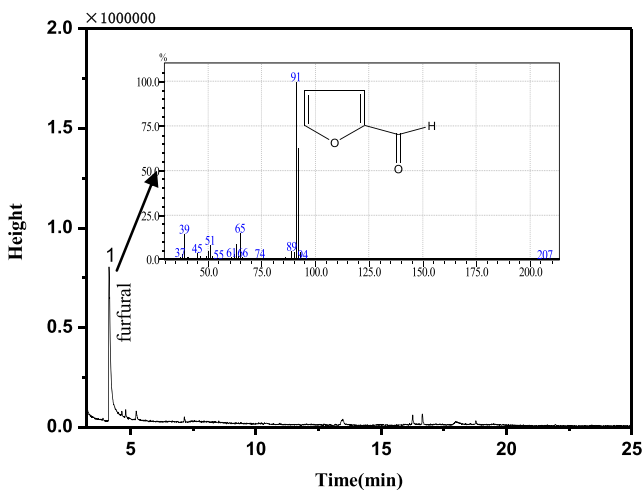


**Fig. 4** Furfural concentration and RS concentration at different temperature



**Fig. 5** The morphology of rape straw residues with a magnification of 1,000 times. **a** Native sample of rape straw. **b** Rape straw residue of at 60 °C. **c** Rape straw residue at 90 °C. **d** Rape straw residue at 110 °C.

**e** Rape straw residue at 130 °C. **f** Rape straw residue at 150 °C. **g** Rape straw residue at 170 °C. **h** Rape straw residue at 190 °C. **i** Rape straw residue at 215 °C. **j** Rape straw residue at 230 °C



**Fig. 6** The GC-MS of liquid production obtained from rape straw (25 ml/min 1.0 % H<sub>2</sub>SO<sub>4</sub> at 110 °C)

They are toxic to yeast growth in the fermentation stage. This is due to timely separation of RS from the reactor.

Finally, aromatic hydrocarbons (with phenolic –OH groups) of lignin are not detected in this study. This proves that no hydrolysis of lignin has taken place. It has been noted that the main hydrolysis of lignin occurs around 400 °C with the formation of aromatic hydrocarbons [34]. In this continuous work, little possibility was provided for massive hydrolysis of lignin.

*FT-IR Analysis*

The chemical structures present in the solid residue of rape straw at each stage changed after hydrolysis reaction. They were investigated using FT-IR spectrum analysis, as shown in Fig. 7. In the FT-IR spectrum, there is no significant distinction between native and 60 °C reacted residue. The broad band at 3,420 cm<sup>-1</sup> is associated with O–H stretching of H bonding

**Table 2** The percentage of all detected matters

Number of peaks	Retention time (min)	Percentage (%)	Compound
1	3.108	89.24	Furfural
2	–	10.76	Other compounds

in cellulose [35]. The peak has no change, indicating that the O–H group exists in all stages.

The peak at  $2,920\text{ cm}^{-1}$  is associated with C–H stretching in aliphatic moieties such as methyl/methylene portions in cellulose [36]. The spectra of a raw sample shows distinct peak at this wavelength. With the increase of temperature, the density of this peak decreases in the temperature range of 60–215 °C. This peak turns to the wave of  $2,850\text{ cm}^{-1}$  at 230 °C, which is attributed to the looseness of the structure in the rape straw. Since the adsorption of bands is diminished in the latter reaction stages, this suggest the exposure of lignin from the compact structure in the straw [37]. All of these indicate that the cellulose is hydrolyzed gradually as the temperature increases. The small shoulder peak at  $1,733\text{ cm}^{-1}$  is associated with the C=O groups that link to the acetyl group in hemicellulose and/or cellulose structure [38]. This evidently decreases from 60 to 110 °C. The absence of this peak after 130 °C implies the removal of most hemicellulose and cellulose.

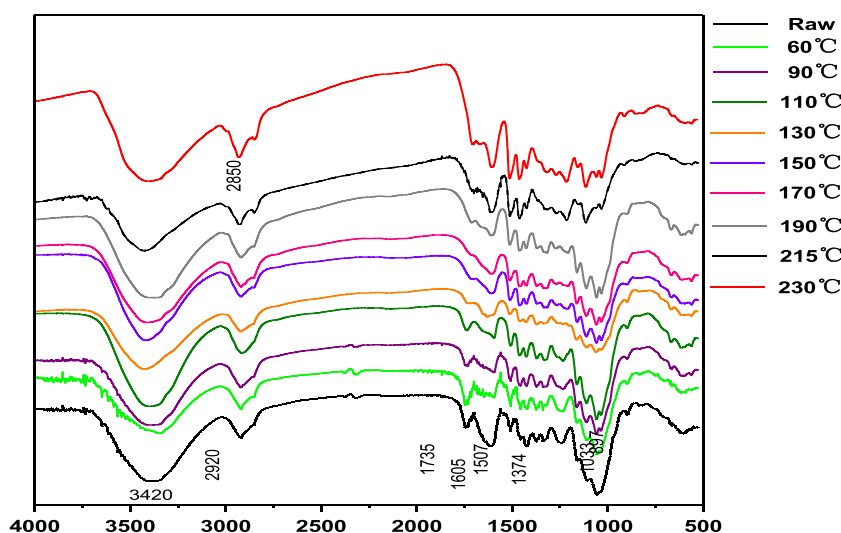
#### The Materials Balance Analysis of Rape Straw

Lignocellulose biomass is mainly composed of three components: cellulose, hemicellulose, and lignin [39]. Cellulose is a linear chain macromolecule with no branch chains. It consists of several hundred to over 10,000  $\beta(1\rightarrow4)$  linked D-glucose units. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighbour chain. In addition, the cellulose in the straw is wrapped by hemicellulose and lignin. All of these factors

determine its rigid structure, so the acid is difficult to reach its surface except for a strong condition. Hemicellulose consists of various sugar units and short molecular chains with many branch chains. It usually has sugar units arranged loosely. Therefore, hemicellulose is easier to be hydrolyzed than cellulose. It was confirmed that the hemicellulose could be hydrolyzed below 100 °C [40, 41]. The lignin is more difficult to be hydrolyzed than the former two. The analysis of three components in the straw is essential in this continuous process.

The main compositions and RS content in different conditions are given in Fig. 8. The material balance for the hydrothermal saccharification of rape straw is measured under optimum conditions [flow rate: 25 ml/min;  $\text{H}_2\text{SO}_4$  concentration: 1.0 % (w/w)]. Rape straw of 100 g was used, which contained 12.69 g hemicellulose, 49.52 g cellulose, and 17.72 g lignin. The hydrolysate and the residues are collected at different reaction stages. Then the RS amount in the liquid is analyzed, and the content of main composition in the residues is also detected.

After reaction at 60 °C, RS of 4.13 g and residues of 89.38 g are obtained which contain 8.78 g hemicellulose, 49.18 g cellulose, and 17.00 g lignin. After reaction at 90 °C, 16.08 g RS and 69.13 g residues are gained. In detail, the amount of hemicellulose, cellulose, and lignin are 2.55 g, 34.91 g, and 15.04 g respectively. After reaction at 110 °C, RS of 8.13 g is collected in the liquid. Residues of 59.13 g are left which contain 1.83 g hemicellulose, 31.72 g cellulose, and 15.04 g lignin. After reaction at 130 °C, 6.83 g RS is gained. The residues are 48.13 g, which contain 1.42 g hemicellulose,

**Fig. 7** FT-IR spectra of original and reacted rape straw

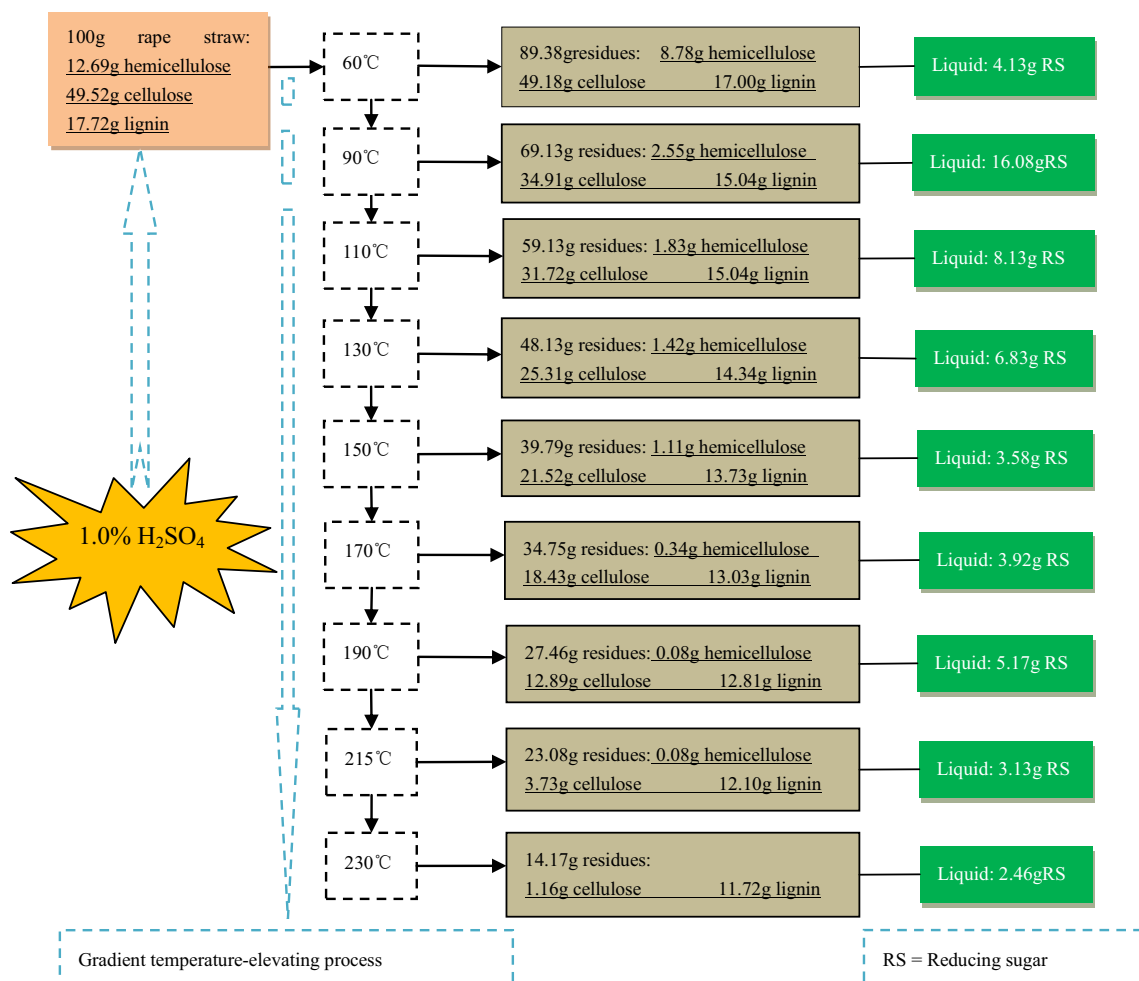


Fig. 8 The material balance for the hydrothermal saccharification of rape straw

25.31 g cellulose, and 14.34 g lignin. After reaction at 150 °C, 3.58 g RS and 39.79 g residues (1.11 g hemicellulose, 21.52 g cellulose, 13.73 g lignin) are collected, respectively. After reaction at 190 °C, 3.92 g RS and 27.46 g residues (0.08 g hemicellulose, 12.89 g cellulose, 12.81 g lignin) are collected in the system. The content of hemicellulose in the residues is very low. During the subsequent reactions at 215 °C and 230 °C, the amount of cellulose further decreased to less than 2.34 %. The hemicellulose is exhausted after reaction at 230 °C. The amount of lignin does not change much.

In Fig. 9, the variation of hemicellulose, cellulose, and lignin is clearly shown. The amount of hemicellulose decreases rapidly. The level of lignin changes is less. The recovery rate of lignin reaches 85.4 %. The amounts of hemicellulose and cellulose decrease step by step along with the stages. The hydrolysis of hemicellulose and cellulose is almost completed below 150 °C, which leads to a high purity of RS, with a conversion ratio of 53.4 %.

On the basis of this sugar yield efficiency, at least 534 kg RS can be obtained from 1,000 kg straw using this method. In China, the available total amount of straw is about 0.85 billion

tons per year. It can be converted to about 0.13 billion tons of ethanol using this approach. It is reported that the amount of

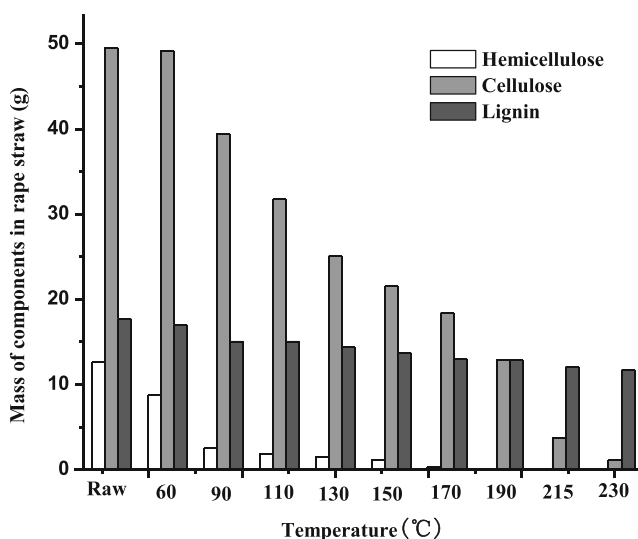


Fig. 9 Three main compositions changing in the hydrothermal saccharification process of rape straw



ethanol required in China is nearly 500 million tons per year. Once the RS produced in a year is converted to ethanol, it is equal to 30 % of the petroleum consumed in China.

## Conclusions

The continuous hydrothermal saccharification of rape straw in dilute H<sub>2</sub>SO<sub>4</sub> medium is demonstrated in this paper. The maximum concentration of RS reaches 20.06 g/l, and the final yield rate is about 53.4 %. The RS is separated immediately after it is produced. Furfural is the only by-product with a concentration lower than 1.06 g/l in this process, which is good for fermentation of RS. The principle of rape straw hydrolysis is as follows: during gradient temperature-elevating process, the hemicellulose hydrolyzes first, then the cellulose hydrolyzes; the lignin is relatively stable and its content does not change evidently. More importantly, the most efficient saccharification process could be completed below 150 °C. A high amount of RS with low toxicity can be obtained by this approach. If all the farm residues are converted to RS in China, 0.13 billion tons of ethanol can be fermented. To conclude, this approach is very promising for alleviating the serious global fossil energy crisis and reducing the emission of greenhouse gases.

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