

Original Research

Transformation Characteristics and Mechanism of Wheat Straw into Organic Acid under Alkaline Hydrothermal Condition

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Abstract

Due to the overuse of fossil energy, fossil energy is facing exhaustion. Agricultural biomass such as wheat straw waste is a kind of clean energy which can replace fossil energy and has important scientific research value and broad application prospect. In this paper, wheat straw was used as raw materials, and the straw was converted into lactic acid, oxalic acid and fumaric acid under alkaline hydrothermal conditions. Improve the yield of organic acid by optimizing the reaction conditions such as NaOH concentration, reaction time and reaction temperature. The optimum reaction conditions were as follows: NaOH concentration 1.5 mol/L, reaction temperature 250°C, reaction time 3 hours, total organic acid yield 13.5%, lactic acid yield 12.1%. The results can provide a new way for the green production of organic acids, and realize the efficient utilization of agricultural waste, reduce environmental pollution. At the same time, can produce good economic benefits, ecological benefits and social benefits.

Keywords: hydrothermal liquefaction, wheat straw, organic acid, biomass

Introduction

China is the largest grain producing country in the world. With the development of grain planting technology, the yield of straw increases simultaneously with the increase of grain production [1, 2]. According

to survey data, the total amount of crop straw resources in China was about 900 million tons, and the amount of straw resources that can be collected and utilized was 680 million tons in 2018 [3]. Different ways of using agricultural straw will have different effects on the environment. If only burning, it will not only waste resources, but also pollute the atmosphere and harm human health [4-6]. Therefore, how to improve the comprehensive utilization level of straw has become a more and more concerned problem. Recent studies

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have shown that the industrialization development of straw resources can greatly promote the overall sustainable development of the region [7].

Wheat is one of the most widely grown crops in China, and its straw contains abundant cellulose, hemicellulose, lignin and other excellent renewable carbohydrates. Organic acids are an important chemical commodity, such as lactic acid, which can treat some inflammatory and immune diseases [8, 9]. The compound of fumaric acid and silver can make wounds heal faster [10]. Using wheat straw as a substrate to produce organic acid can not only realize the resource utilization of biomass waste, but also increase the economic benefits of crops [11, 12]. Traditional organic acid production methods include fermentation, chemical synthesis and so on [13, 14]. Although these methods can achieve a high conversion rate, the steps are complicated, the cost is high, and the time is long. The gaseous or liquid substances generated in the production process are easily discharged into the environment, causing environmental pollution. Therefore, seeking a low pollution and high efficiency method to produce organic acids is the only way to achieve green production of organic acids.

A large number of studies have shown that selecting appropriate pretreatment can break the crosslinking between lignin, hemicellulose and crystalline cellulose in straw, improve its conversion efficiency and obtain higher product benefits [15-19]. Among the pretreatment, hydrothermal treatment is an environmentally friendly process. Compared with the traditional fermentation method, the hydrothermal treatment method is simpler and faster. Hydrothermal treatment can improve the pre-hydrolysis of organic matter in straw and produce solid and liquid rich in sugar. At the same time, alkali treatment will destroy the hydrogen bond in cellulose, and the spatial distance between cellulose increases, so that the composition, structure and properties of fiber are changed, and more free surface is exposed, with larger water and specific surface area and pore volume [20-22]. These two aspects can greatly promote the transformation of lignin and cellulose. Compared with untreated raw materials, the combined saccharification rate of alkaline hydrothermal treatment is significantly increased [23]. However, the promotion effect of alkaline hydrothermal environment on the conversion of crop straw into organic acid is rarely reported.

In this study, wheat straw was used as raw material and alkaline hydrothermal treatment method was adopted to explore the combination of optimal NaOH concentration, reaction temperature and reaction time for conversion of straw biomass into organic acid. Wheat straw with low added value was transformed into organic acid with high added value, reducing environmental pollution and improving ecological environment also provide a new green way for organic acid production, realize the efficient use of agricultural wastes such as wheat straw, and use waste straw biomass resources to meet the growing material needs

of people in society to a great extent, produce good economic benefit, ecological benefit and social benefit.

Materials and Methods

Experimental Materials

Methanol used in this experiment ($\geq 99.9\%$, Shanghai Star High Purity Solvent Co., Ltd.), Lactic acid (1 M, Sigma), Fumaric acid ($\geq 99.0\%$), pyruvate ($\geq 98.5\%$), glycolic acid ($\geq 99.5\%$), formic acid ($\geq 98.0\%$) and phosphoric acid ($\geq 85\%$) were purchased from Sinopharm Chemical Reagents Co., Ltd. Concentrated sulfuric acid ($\geq 95.0\%$), sodium hydroxide ($\geq 96.0\%$), anhydrous sodium sulfate ($\geq 99.8\%$), sodium chloride ($\geq 99.5\%$), methylene chloride ($\geq 99.5\%$) were purchased from Xilong Scientific Co., Ltd. Wheat straw was taken from the farmland of Lujiang experimental station of Anhui Agricultural University (Anhui, China). Wheat straw after grinding through 80 mesh sieve (mesh size: 0.18 mm, Zhejiang Shangyu Jinding standard sieve factory, China).

Experimental Methods

All experiments were carried out in a 27 mL teflon lined stainless steel batch reactor (Wuxi Nanfang Seiko automobile maintenance machinery factory, China). During the experiment, reagents such as NaOH, wheat straw (0.8 g through 80 mesh sieve) and water (10 ml) were added to the reactor and sealed, and then put into the oven (DHG-9078A, Shanghai Jinghong Experimental Equipment Co., Ltd., China) preheated to the required temperature for reaction. After the reaction reached the set time, the reactor was taken out and cooled to room temperature, and then liquid samples were collected. The liquid samples were filtered by 0.22 μm membrane and analyzed by HPLC (STI-501, Sage Technology Co., Ltd. Hangzhou, China) and GC-MS (Trace GC+ITQ 1100, Thermo Fisher, USA), respectively. The wheat straw was analyzed by using Vario EL Cube (German element analysis system, Germany) automatic elemental analyzer.

Test Method

The low molecular weight organic acids (oxalic acid, fumaric acid and lactic acid) in the liquid samples were determined by high performance liquid chromatography (STI-501, Sage Technology Co., Ltd. Hangzhou, China). The detection conditions were as follows: two Shodex KC811 columns in series with 0.1% H_3PO_4 mobile phase at the flow rate was 1.0 mL/min, injection volume 10 μL , column temperature 50°C, UV detector. The liquid samples were esterified by sulfuric acid-methanol solution and analyzed by GC-MS [24]. The elemental analysis conditions of wheat straw were as follows: injection quantity: 5 mg, detection time:

Table 1. Contents of Elements in Wheat Straw (80 mesh).

Contents of various elements in wheat straw (80 mesh)				
N (%)	C (%)	H (%)	C/N	C/H
0.628	38.652	5.775	61.548	6.693

90 s, determination accuracy: relative deviation of C, H and N were $\leq 0.1\%$, decomposition temperature: 950°C . Basic properties of wheat straw elements are shown in Table 1.

In this paper, the organic acid yield is defined as the percentage of the carbon content of an organic acid in the liquid phase mixture to the total carbon content of the added wheat straw:

$$\text{organic yield}(\%) = \frac{\text{carbon amount in organic acid in liquid mixture after reaction}}{\text{total carbon amount in added straw}} \times 100\%$$

Results and Discussion

Effect of NaOH Concentration on Organic Acid Production from Wheat Straw

Fig. 1 shows the effect of NaOH concentration on the hydrothermal conversion of wheat straw into organic acids. As can be seen from Fig. 1, when NaOH is not added, the yield of lactic acid in the liquid phase after straw hydrothermal reaction is only 0.4%, and the yield of oxalic acid and fumaric acid are both less than 0.1%. With the increase of alkali concentration, the yield of lactic acid, oxalic acid and fumaric acid in the liquid phase after reaction shows a trend of first increasing and then decreasing. When the alkali concentration was 1.5 mol/L, the maximum yield of total organic acid was 9.4%, among which, the yield of lactic acid and

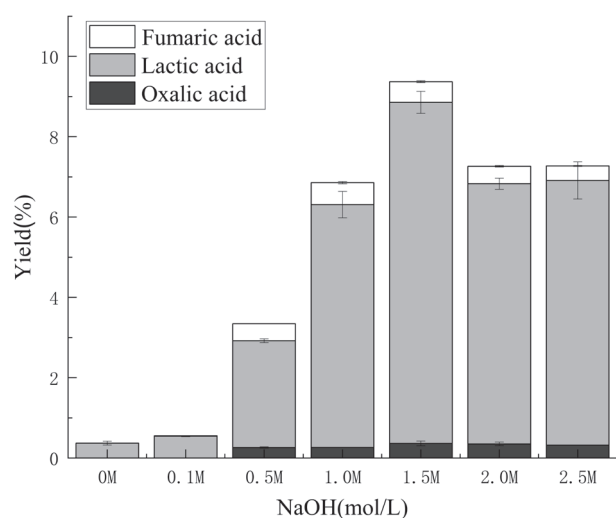


Fig. 1. Effect of NaOH concentration on hydrothermal conversion of wheat straw to organic acid (Reaction conditions: straw 0.8 g, Reaction temperature: 230°C , Reaction time: 3 h).

oxalic acid were 8.5% and 0.4%, respectively. The total organic acid yield decreased as the base concentration continued to increase. The total yield of lactic acid, oxalic acid and fumaric acid produced by hydrothermal reaction of 2.0 mol/L NaOH solution with straw was 7.3%, in which the yield of lactic acid was 6.5%, oxalic acid was 0.4% and fumaric acid was 0.4%. When the alkali concentration was increased to 2.5 mol/L, the total yield was 7.3%, which was not much different from the total organic acid yield when the alkali concentration was 2 mol/L.

Alkali treatment can promote the decomposition of cellulose hemicellulose and lignin [25-27]. The removal of lignin and hemicellulose by adding chemicals or solvents was more significant than by adding water alone [27]. Therefore, in the hydrothermal treatment, adding an appropriate amount of alkali can effectively improve the yield of various organic acids. At the same time, alkali concentration should not be too high, otherwise it may reduce its yield, resulting in a waste of resources, but also to the environment caused by certain pollution.

Effect of Reaction Time on Organic Acid Production from Wheat Straw

Fig. 2 shows the effect of reaction time on the conversion of wheat straw into organic acids. As can be seen from Fig. 2, when the reaction time increased from 120 min to 210 min, the total organic acids in the reaction system showed a trend of first increasing and then decreasing. When the reaction time was 120 min, the total yield was 4.6%. When the reaction time increased to 180 min, the total organic acid yield reached the maximum value of 9.4%. When the reaction time continued to increase to 210 min, the yield of organic acids showed a decreasing trend.

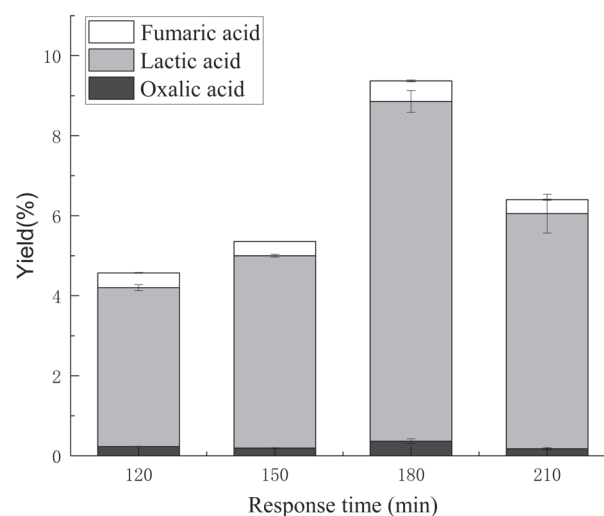


Fig. 2. Effect of reaction time on conversion of wheat straw into organic acid (Reaction conditions: straw 0.8 g, NaOH 1.5 mol/L, Reaction temperature 230°C).

Under hydrothermal conditions, with the increase of reaction time, the decomposition of cellulose and hemicellulose in wheat straw became more complete, and the yield of oxalic acid, lactic acid and fumaric acid in liquid phase increased continuously. However, when the reaction time is more than 3 hours, as the reaction time continues to increase, the conversion rate of wheat straw into organic acids is less than the decomposition rate of organic acids, so the organic acid yield decreases. The reaction time for producing organic acids is mainly related to the properties of raw materials used under given conditions in the hydrothermal process [28]. Therefore, in the experimental production process, we need to control the reaction time according to the different experimental materials and conditions, so that the raw materials can be transformed into the required products as much as possible.

Effect of Reaction Temperature on Organic Acid Production from Wheat Straw

Fig. 3 shows the effect of reaction temperature on the conversion of wheat straw into organic acids. As can be seen from Fig. 3, with the increasing reaction temperature, the total organic acid yield shows an increasing trend. When the temperature was 185°C, the total organic acid yield was 2.7%. When the temperature was 200°C, the total organic acid yield was 3.9%. When the reaction temperature increased to 250°C, the total organic acid yield reached the highest 13.5%.

Straw decomposition and transformation could be promoted by increasing temperature [29, 30], therefore, with the increase of reaction temperature, straw hydrothermal transformation is more sufficient. At lower temperatures, the reaction temperature has little effect on the yield, total organic acid production rate is low. Reaching a certain temperature, the straw began a large

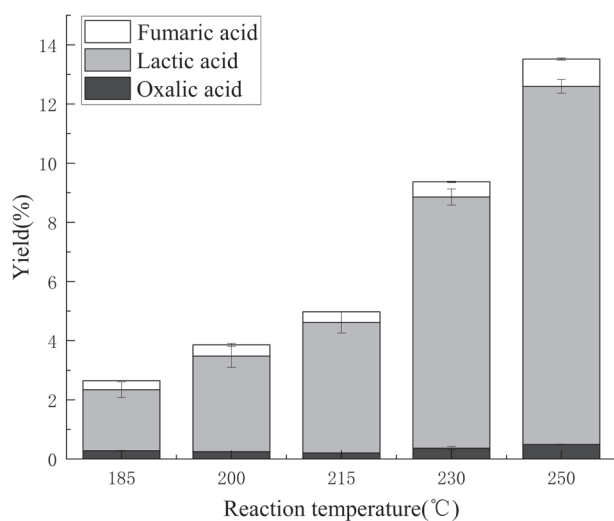


Fig. 3. Effect of reaction temperature on conversion of wheat straw into organic acid (Reaction conditions: straw 0.8 g, NaOH 1.5 mol/L, Reaction time 3 h).

number of decomposition, macromolecular substance in the transformation to generate other substances, the yield of organic acids increased greatly.

The presence of crosslinking between cellulose and lignin may hinder the hydrothermal conversion degree of straw, and the binding of cellulose, hemicellulose and lignin is destroyed by temperature increase [31]. Therefore, the increase of temperature is conducive to the decomposition of cellulose and makes it easy to hydrolysis [32, 33], so as to increase the yield of organic acids. However, the temperature should not be too high, in too high temperature conditions, lignin in the solid matrix condensation [34], thus its conversion rate will also be reduced.

Reaction Mechanism of Straw Conversion to Organic Acid under Alkaline Condition

Cellulose, hemicellulose and lignin are the main components of straw. Cellulose has a tight microfibril structure, with β -1, 4-glycosidic bonds linked into linear chains of D-glucose units as the main building blocks. Lignin is associated with cellulose and hemicellulose for mechanical strength [27]. Under alkaline hydrothermal conditions, wheat straw degrades into xylose oligosaccharides, xylose, furfural and other by-products. In this process, lignocellulosic structure crosslinking is broken, and alkaline catalyst can promote the condensation of cellulose, hemicellulose and their monosaccharides to form intermediate compounds, such as glyceraldehyde and pyruvaldehyde. Lignin breaks down to produce guaiacol. All of these substances eventually produce organic acids [28].

HPLC analysis of liquid products after hydrothermal reaction of wheat straw under alkaline conditions (Fig. 4) shows that organic acids in liquid products included oxalic acid, lactic acid and fumaric acid, among which the content of lactic acid was the highest. Fumaric acid has the highest peak, but its concentration

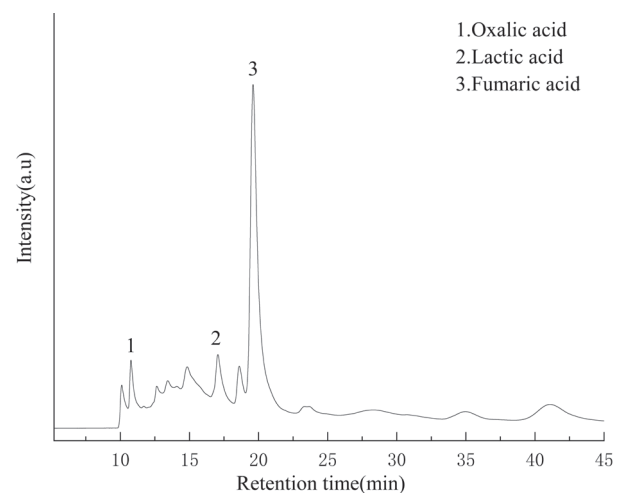


Fig. 4. HPLC analysis of liquid phase products after straw hydrothermal reaction (Straw: 0.8 g, NaOH: 1.5 M, 230°C, 3 h).

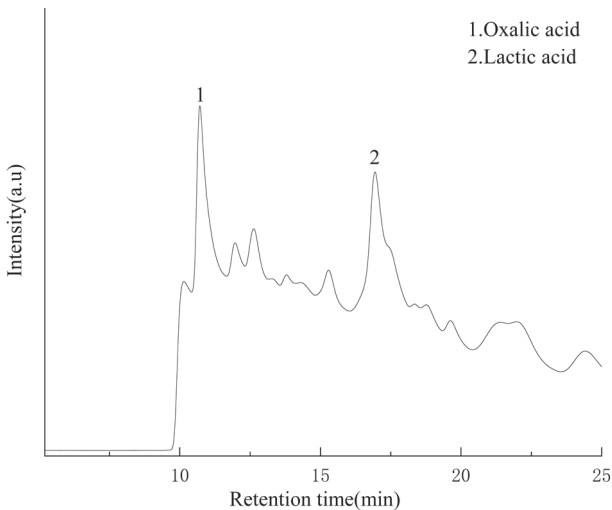


Fig. 5. HPLC analysis of liquid products after hydrothermal reaction of acetone aldehyde (Pyruvic aldehyde: 0.5 M, NaOH: 1.5 M, 230°C, 1 h).

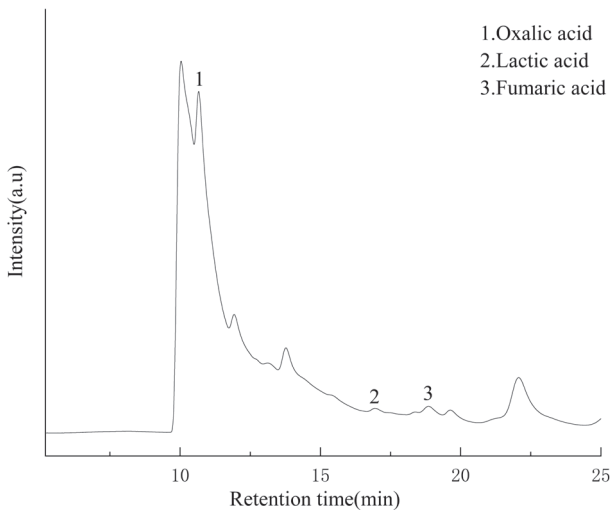


Fig. 6. HPLC analysis of liquid phase products after hydrothermal reaction of guaiacol (Guajacolum: 0.5 M, NaOH: 1.5 M, 230°C, 3 h).

is not high. After hydrothermal reaction with pyruvate aldehyde, the intermediate product of cellulose hydrolysis, HPLC analysis was performed on the liquid products (Fig. 5). It was found that the organic acids mainly included lactic acid and oxalic acid, so it could be concluded that part of lactic acid and oxalic acid generated in the liquid products came from the decomposition and transformation of cellulose. Fig. 6 shows the HPLC analysis of guaiacol after hydrothermal reaction. It was found that the organic acid products included oxalic acid, lactic acid and fumaric acid. Therefore, it was inferred that part of oxalic acid, lactic acid and fumaric acid in the liquid product after straw reaction were generated by the hydrolysis of guaiacol.

To sum up, the pathway of wheat straw to produce organic acids through hydrothermal transformation under alkaline conditions (Fig. 7): Cellulose is decomposed into glucose monomer under alkaline hydrothermal conditions. With the progress of the reaction, it continues to be transformed into glyceraldehyde, and then into pyruvate, oxalic acid and other organic acids [28, 35]. Lignin will decompose into guaiacol under the same alkaline hydrothermal conditions, and then generate lactic acid, oxalic acid and fumaric acid and other organic acids, but its organic acid yield is much lower than cellulose.

Conclusions

In this paper, a method of hydrothermal transformation of wheat straw to produce organic acids under alkaline condition was proposed. Under the condition of alkali concentration of 1.5 mol/L and reaction temperature of 250°C for 3 hours, the total yield of lactic acid, oxalic acid and fumaric acid can reach 13.5%. Among them, lactic acid is the organic acid with the highest yield, and the highest yield is 12.1%. This method can provide a new idea for efficient utilization of agricultural biomass waste resources.

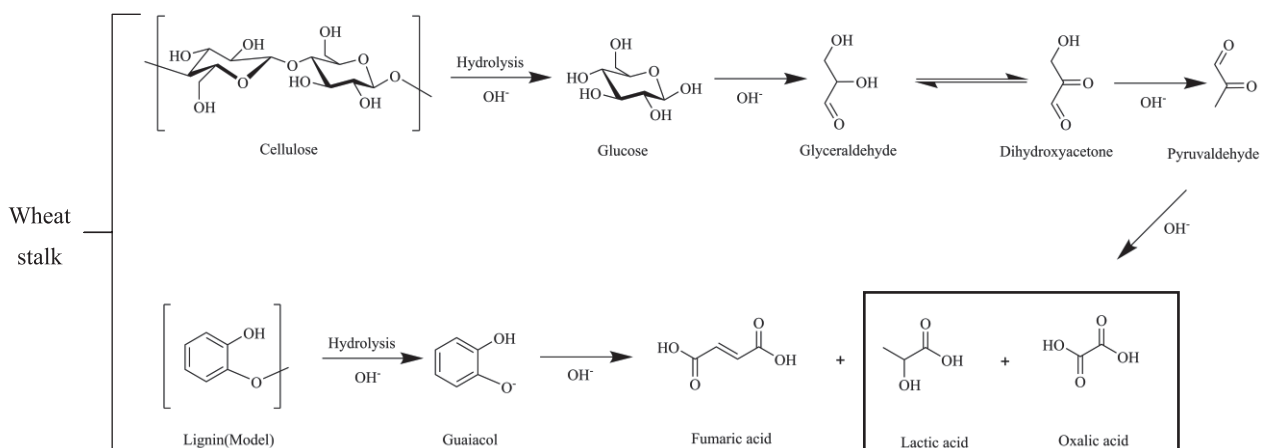


Fig. 7. Reaction mechanism diagram of straw hydrothermal conversion to organic acid.

The process of straw hydrothermal conversion is complicated and the reaction mechanism needs to be further improved. In addition to several organic acids mentioned in this paper, there should also be other compounds in the reaction products. It is also important to further confirm the composition of reactants and study whether there are other valuable transformation ways of wheat straw. Compared with the traditional method of chemical synthesis of organic acids, this study uses waste wheat straw as raw material to produce organic acids by simple hydrothermal transformation, which not only provides a more convenient and fast new idea for the production of organic acids, but also has important significance for promoting the sustainable development of agriculture.

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Conflict of Interest

The authors declare no conflict of interest.

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