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An Analysis of Pre-treatment Methods of Wheat Straw

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Abstract: By taking the reducing sugar yield as an evaluation standard, this research compared and evaluated the various pre-treatment methods available for the processing of wheat straw. Based on this analysis, the optimal pre-treatment method and its optimisation conditions, for wheat straw were proposed. This research provided a reference for wheat straw ethanol pre-treatment technology applicable to both researchers and producers. A comparative analysis showed that wheat straw pre-treated by a phosphoric acid method can save energy, reuse waste water, etc. The reducing sugar yield reached 70.3%. It also can optimise a propionic acid pre-treatment method by using ultrasonic and propionic acid pre-treatment methods combined. In addition, the production cycle can be shortened, moreover, by using the method proposed, 88.4% of the high reducing sugar yield can be obtained.

Key words: Wheat straw, pretreatment, lignocellulose, evaluation

INTRODUCTION

Many countries such as Brazil and USA, have used the biomass energy from corn, wheat and sugar cane to produce fuel ethanol: however, in China, as elsewhere, food supply/security is still an issue so using grain as a raw material to produce fuel ethanol is limited (Zhang *et al*., 2009). However, due to favourable characteristics such as renewability and non-polluting characteristics, the use of lignocellulosic biomass as a raw material to produce fuel ethanol has been widely studied and applied (Liu *et al*., 2009; Liu *et al*., 2005; Varga *et al*., 2003; Akpinar *et al*., 2004; Zhang and Lynd, 2003; Moiser *et al*., 2005; Gottschalk *et al*., 2009).

The main steps in using lignocellulose to produce fuel ethanol consist of: pre-treatment, hydrolysis, fermentation and the isolation and purification of the product (Singh *et al*., 2009; De Vrije *et al*., 2002; Jorgensen *et al*., 2007). Among which, the pre-treatment is the key technology when transforming cellulose to fuel ethanol (Lu *et al*., 2009; Weil *et al*., 1994; Nakamura, 2005; Chosdu *et al*., 1993; Wang *et al*., 2008; Mosier *et al*., 2005). It is regarded as essential in improving the accessibility of materials, enhancing production efficiency and reducing production cost.

THE NEED FOR LIGNOCELLULOSE MATERIAL PRE-TREATMENT

Owing to its complex chemical composition and multi-level compact structure, lignocellulosic materials are difficult to biodegrade (Hansen *et al*., 2011; Mandels and Sternberg, 1976). As with other lignocellulosic materials, wheat straw is easily available and rough. Hydrogen bonding plays a major role in the combination of cellulose molecules and hemicellulose molecules, or the coalescence of lignin molecules. There are still other main bonds between the hemicellulose and lignin molecules such as: ether bonds, ester bonds, glycoside bonds and acetal bonding. There is no chemical chain between the cellulose, hemicellulose or lignin molecules at all. However, the chemical chain can combine hemicellulose and lignin molecules into a complex which can tightly surround the cellulose molecule with hydrogen so as to make the cellulose molecule difficult to be hydrolyzed. This research showed that the hydrolysis rate of raw material without pre-treatment was lower than 20 but it improved to over 90 %with pre-treatment (Mandels *et al*., 1976). The pre-treatment can change the compact structure; destroy the chemical and physical chains so as to reduce the crystallinity of the cellulose. It can also remove lignin and increase raw material osteoporosity to increase the effective contact with the cellulose system. The typical chemical composition of wheat straw is shown in (Table 1).

Table 1: Main components of wheat straw

	Component			
Parameter	Cellulose	Hemicelluloses	Lignin	Ash content
Percentage (%)	51.16	23.69	21.21	2.76

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THE INFLUENCE OF PRE-TREATMENT ON WHEAT STRAW

The physics

Radiation treatment: Radiation processing technology is defined as: a radiolysis reaction, which uses Y-rays from radioisotopes such as cobalt-60 or cesium-137, or an electron beam produced by an electron accelerator to induce degradation of cellulose. Under Y-, or high-energy electron, radiation carbohydrates in plant tissues and their combination with lignin will be destroyed: this is one of the reasons why cellulosic polysaccharide is easily hydrolyzed (Zou *et al*., 2011; Zhu, 2005; Tang *et al*., 2011).

Wheat straw was γ-irradiated to a dose of 100 kGy, then soaked in 2% NaOH aqueous solution for 1 h. The optimal enzymolysis conditions for pre-treating wheat straw were: an enzyme substrate of 50 mg g^{-1}, a substrate of 1 g 50 mL^{-1} buffer, a temperature of 50°C and a pH of 4.8. The reducing sugar yield of the wheat straw can reach 80.15% under such conditions.

The chemistry

Acid treatment: Acid treatment is a common lignocellulose pre-treatment method: it can improve hemicelluloses hydrolysis and destroy the crystalline structure of cellulose so as to loosen the structure of raw materials, which can improve the fermentability of cellulose. Dilute sulphuric acid, concentrated sulphuric acid, propionic acid and phosphoric acid are usually used to treat wheat straw.

The treatment of dilute sulphuric acid: Dilute sulphuric acid, is used to pre-treatment the lignocellulose raw material. It not only hydrolyzes cellulosic materials but destroys the crystallisation structure thereof. This leads to a looser structure of the raw material and improves the fermentability of the cellulose.

This research presented the effects of reaction time, acid concentration and temperature on the hydrolysis of wheat straw (Qiang *et al*., 2010; Chen *et al*., 2009). The optimal conditions for hydrolysis at relatively low temperatures are a solid-liquid ratio of 1:8 and a dilute acid concentration of 0.6%. The reducing sugar concentration was 50.34 g L^{-1} and the yield is 61.96% at 160°C for 1 h.

However, the treatment of the wheat straw using treating sulphuric acid showed an obvious defect: difficulties in recycling raw materials increased the cost of pre-treatment; meanwhile, sulphuric acid was likely to corrode the reaction vessel and damage the equipment.

Propionic acid treatment: Propionic acid is a type of lower fatty acid, which has the characteristic of being able to degrade lignocellulosic raw materials. The straw and other cellulose polymers, are degraded into cellulose, hemicellulose and lignin: complete utilisation of biomass can be therefore realised. The reaction conditions under which propionic acid degraded straw were mild. Propionic acid can degrade straw at atmospheric pressure and relatively low temperatures (115°C) without high voltage equipment. Compared with traditional processes, it was deemed superior on these grounds (Tian and Ma, 2011; Tian and Ma, 2012).

The optimal technological conditions defined by these tests were: a liquid ratio of 1:16, a propionic acid mass concentration of 900 g L^{-1}, a catalyst mass concentration of 3 g L^{-1}, a temperature of 70°C and a treatment time of 150 min. Under these conditions, the cellulose retention rate of wheat straw was 92.6%, the removal rates of hemicellulose and lignin were 98.3 and 70.5%, respectively. After pre-treatment, the enzymolysis rate of wheat straw was 90.3%, which exceeded that of the conventional dilute acid pre-treatment method.

Phosphoric acid treatment: Phosphoric acid with a purity of 85% (w/w) can pre-treat wheat straw under atmosphere pressure. Different straw particle sizes, solid-liquid ratios, temperatures, reaction durations and other pre-treatment conditions had different effects on the wheat straw enzymatic scarification rate (Gong *et al*., 2008; Karimia *et al*., 2006).

The optimal condition for wheat straw pre-treatment defined by test was a particle size passing the 60 No. mesh, a solid-liquid ratio of 1 .0:8.5, a temperature of 70°C and a reaction time of 1 h. After pre-treatment of wheat straw before enzymatic hydrolysis under these conditions, the enzymatic scarification rate increased to 70.3%.

The enzymatic scarification rate of wheat straw pre-treated by phosphoric acid increased significantly and exceeded that for straw pre-treated by dilute acid. The enzyme reaction time for wheat straw degraded by phosphoric acid was short. Phosphoric acid pre-treatment produced a by-product waste liquid which could be a precursor for the production of phosphate fertiliser. Therefore, it was a low-energy, effective and environmentally friendly pre-treatment method. It can provide technical support for the wheat straw ethanol chemical industry.

Alkaline treatment: NaOH is regarded as the most widely used, earliest discovered and most effective substance for pre-processing plant cellulose material. It is known that β-glucoses can obtain about 20% yield when hydrolyzing wheat straw with the best alkali concentration at 1% (w/w) (Liu *et al*., 2013). Only a low sugar yield can be achieved when alkali treatment was used because destruction of the NaOH in the lignin ester bond increased the porosity of the straw, which engendered the difficulty in cellulose hydrolysis.

Table 2: Sugar yield comparison of pre-treated wheat straw

	Treatment						
Parameter	Radiation	Dilute sulphuric acid	Propionate	Phosphate	Alkali	Ultrasonic mild alkaline oxidation	Ultrasonic synergistic acid
Sugar yield (%)	80.15	61.96	90.3	70.3	20.0	62.6	88.4

Physico-chemical pre-treatment

Ultrasonic and mild alkaline oxidation treatments: A mild alkaline oxidation ultrasound-assisted method of treating wheat straw to degrade lignin was undertaken by applying the high lignin removal of mild alkaline oxidation and the short duration of the ultrasound-assisted method (Yang *et al*., 2007). This provided a theoretical basis for the technology. In this research, the optimal conditions for treatment were: a NaOH concentration of 1.54%, an ultrasonic power of 1160W, for a duration of 50 min and an initial water temperature of 78 to 69°C. The relative content of lignin, pre-treated thus, was the minimum (8.22 %) with a reducing sugar yield of 72.6%.

Ultrasonic and propionic acid treatment: Pre-treatment with ultrasonic and propionic acid can strip hemicellulose and lignin from straw as much as possible, which can expose the cellulose and is conducive to the subsequent enzymatic hydrolysis and ethanol fermentation. Propionic acid, which can be recycled by vacuum distillation or other methods, can avoid environmental contamination (Feng *et al*., 2009; Ahamed and Vermette, 2010). The optimal conditions defined by test were: a liquid ratio of 1:12, a propionic acid concentration of 900 g L^{-1}, a catalyst concentration of 3 g L^{-1}, ultrasonic power of 300W for a reaction time of 15 min. Under these conditions, the retention rate of the cellulose of wheat straw was 91.4%; the reducing sugar yield rate by enzymatic hydrolysis was 88.4%.

COMPARATIVE ANALYSIS OF PRE-TREATMENT METHODS

Analysis of the reducing sugar yield: The yield of lignocellulosic enzyme sugar was improved with the seven aforementioned pre-treatment methods for wheat straw. Based on the analysis of these methods, the conclusion is drawn in (Table 2).

The Table 2 shows that the best pre-treatment for sugar was phosphate treatment whereas alkaline treatment yielded 20.0% sugar.

The applicability of the methods: The pre-treatment method of wheat straw cannot be chosen solely by sugar yield level evaluation, but should be based on the specific circumstances considering multiple factors. To carry out production and create profit, it is reasonable to choose a pre-treatment according to differing characteristics.

The analysis showed that radiation treatment could achieve an eco-friendly, high yield of sugar of 80.15% using only simple operations for a short time. The radiation-based operations must be rigorously controlled, meanwhile, the waiting time after initial radiation makes the production cycle much longer despite the shorter pre-treatment times. Wheat straw treated with sulphuric acid technology was a better-established, simpler, method; however, it had one obvious shortfall: difficulties in recycling the materials incurred more cost. Furthermore, sulphuric acid can corrode the reaction vessel and damage the instrument. Pre-treatment using propionate was an ideal treatment because of its weak causticity and easy recovery. Phosphate was more eco-friendly than propionate because the waste could also be used as a precursor for phosphate fertiliser manufacture. Alkali treatment was not recommended because its sugar yield was so low and the waste difficult to handle. Ultrasonic assistance of both physical and chemical treatments could avoid the long production cycle of propionate and phosphate treatments. The new method appeared promising.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

An appropriate pre-treatment method, according to different production requirements, was selected.

- When budget constraints are present, cheaper pre-treatment methods such as propionic acid or phosphoric acid may be used: phosphoric acid was the preferred pre-treatment when better reducing sugar yield, waste utilisation, eco-friendliness, etc. were required. The best conditions for pre-treatment consisted of: a particle size such that it passed a 60 No. mesh, a solid-liquid ratio of 1.0:8.5, a temperature at 70°C and a reaction time of 1 h. Under such conditions, the enzymatic scarification rate reached 70.3% when pre-treatment was conducted before the enzymatic hydrolysis of wheat straw
- When the budget permits, pre-treatment with physico-chemical processes was preferred because, after carrying out ultrasound-assisted treatment, these methods can shorten the production cycle and retain a high reducing sugar yield after acid treatment

at the same time. The best conditions for ultrasound-assisted propionic acid pre-treatment were: a solid-liquid ratio of 1:12, a propionate concentration of 900 g L^{-1}, a catalyst concentration of 3 g L^{-1}, an ultrasonic power of 300W and a reaction time of 15 min. Under these conditions, the reducing sugar yield, after enzymatic hydrolysis, reached 88.4%

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