

Enhanced Fermentable Sugars Yield for Bioethanol Production from Lignocellulosic Biomass

Wimonrat Tongpoorthorn, Kamonchanok Konglun and Natnarin Seeto

Department of Chemistry, Faculty of Engineering, Rajamangala University of Technology
Isan, Khon Kaen Campus, Khon Kaen, Thailand, 40000

aammyytt@hotmail.com

Abstract. *The three pretreatment methods to enhance fermentable sugar yield for bioethanol production from corn stalk including acid pretreatment method(1), acid-ultrasonication pretreatment method(2) and acid-autoclave pretreatment method(3) were investigated. Chemical composition analysis of pretreated corn stalks were carried out using FT-IR technique and standard TAPPI method. The results showed that all pretreated samples consist of mainly cellulose, which is basic unit of sugars that can be fermented into ethanol. The maximum cellulose content of 68.15%wt, 82.20%wt and 78.47%wt were obtained from method (1), (2) and (3), respectively. Although, a quite similar fermentable sugar yield, determined by DNS method (30.51-32.94mg/mL), for all samples was observed. However, it was indicated that using ultrasonication and autoclave in pretreatment process could significantly reduce time consuming than that of only acid pretreatment. The morphological features and surface characteristics of all pretreated samples determined by SEM evident that the complex structure of sample was decomposed resulted in fermentable sugar release. In conclusion, acid-autoclave pretreatment was considered as appropriated method in this work. It can enhance fermentable sugar yield with short time and low energy required for proceed. In addition, this method is mild operating conditions, simple to perform and environmentally friendly processing.*

Keywords:

Bioethanol, lignocellulosic biomass, pretreatment, fermentable sugar, corn stalk

1. Introduction

Current world bioethanol research is driven by the need to reduce the costs of production. For example, improvement in feedstock pretreatment, finding a low-cost and renewable feedstock, especially for agricultural waste. Lignocellulosic biomass (a complex comprised of several polysaccharides) is the most promising feed stock considering its great availability and low cost [1]. The lignocellulosic biomass is formed by three structural polymer: cellulose, hemicelluloses and lignin. Moreover, it

has small quantities of other compounds. Among these components, carbohydrate (cellulose and hemicelluloses) can be saccharified and eventually fermented to obtain bioethanol. This becomes an interesting alternative to reduce competition with the food industry and to generate an added value to the agro-industrial residues [2]. Among variety of lignocellulosic biomass, corn was chosen because it is the most widely grown in Thailand. Only a small portion of corn is used for animal feed and bedding or for industrial use, most of corn is still left on the fields or disposed of as waste (corn stalk). Promoting the use of corn stalk as a raw material for bioethanol production could help increase the cellulosic ethanol production in Thailand and reduce the quantity of biomass that goes to waste. However, the complete process to produce bioethanol from lignocelluloses is more complex than usual production via fermentation of sugar, which demands more optimization [3]. Hence, pretreatment of biomass is always necessary to remove and/or modify the surrounding matrix of lignin and hemicellulose prior to the hydrolysis of the polysaccharides in the biomass [4]. Pretreatment has been views as one of the most expensive processing steps within the conversion of biomass to fermentable sugars (reducing sugar). The selection of an appropriate pretreatment technique remains one of the major challenges in developing economically viable technologies for bioethanol production. Although, several different pretreatment methods for corn have been studied in the past [5, 6], but no method has yet emerged as being efficient, but also simple and cost effective. From this point of view, ultrasonication and autoclave methods were applied in pretreatment step in combination with dilute acid to enhance fermentable sugars yield. These methods also expect to have great potential for the improvement of efficiency and reduction of cost.

2. Experimental

2.1 Raw Material

Corn stalk was used as raw material in this study. It was obtained from local area in Khon Kaen province of

Thailand. It was dried in the oven at 80°C for 48 h. The dried sample was crushed with a blender and sieved to a size smaller than 2 mm. The sample was stored in a sealed plastic bag and used throughout the experiment.

2.2 Pretreatment

2.2.1 Acid pretreatment method

Sample of the mixture of corn stalk and 2% v/v H₂SO₄ at the ratio of 1:12.5 w/v was placed in the screw cap glass bottom and then subjected to pretreat by impregnation at ambient temperature under optimized condition (1 day), determined in the previous experiments. After that, the mixture was filtered. A liquid portion was then determined reducing sugar content by DNS method whereas a solid portion was analyzed chemical compositions by FT-IR technique and TAPPI method. Furthermore, the morphological features and surface characteristics of materials were also studied using Scanning electron microscopy (SEM).

2.2.2 Acid-ultrasonication pretreatment method

Sample of the mixture of corn stalk and 2% v/v H₂SO₄ at the ratio of 1:12.5 w/v was placed in the screw cap glass bottom and then subjected to pretreat by ultrasonication under optimized condition (10 min), determined in the previous experiments. The ultrasonication was carried out in a sonicator (Model: Power sonic 410, power 500 W, Hwashin Technology, Seoul, Korea). The mixture was filtered and analyzed as same as the method in mention above.

2.2.3 Acid-autoclave pretreatment method

Sample of the mixture of corn stalk and 2% v/v H₂SO₄ at the ratio of 1:12.5 w/v was placed in the screw cap glass bottom and then subjected to pretreat by autoclave under optimized condition (15 psi for 10 min), determined in the previous experiments. The autoclave pretreatment was performed in autoclave (Model H-88LLD, Kokusan, Japan). The mixture was filtered and analyzed as same as described in mention above.

2.3 Analytical methods

The surface functional groups of all samples were analyzed by using FT-IR spectroscopy (Perkin-Elmer, Spectrum One model Spectrometer, England). The sample spectra were obtained using 60 scans of the samples with resolution of 4 cm⁻¹ in the range of 450-4000 cm⁻¹. The samples were prepared by KBr pellet method. The content of chemical compositions of the samples was analyzed by standard TAPPI method [7]. Total fermentable sugars were determined by the DNS method [8] using UV-VIS spectrophotometry (JESCO V-530 model, Analytical Lab.

Science Co., Ltd, Thailand). Glucose was used as the standard in this method. Scanning electron microscopy (SEM) was used for study of the effect of pretreatment on physical properties change in the biomass. The freeze dried samples were placed on carbon taps and subjected to the high performance scanning electron microscope (JSM-6480LV model, JEOL, Japan).

3. Results and Discussions

3.1 Chemical compositions

FT-IR spectra of all pretreated samples are presented in Fig.1. It was found that all samples show the transmittance around 897 cm⁻¹, which is assigned to β-glucosidic linkages in cellulose and hemicelluloses. Lignin characteristic can be followed by the peaks at 1218 cm⁻¹ (C-O of guaiacyl ring). Moreover, peak at 1650 cm⁻¹ indicated C=O carbonyl group with intra- and intermolecular hydrogen bonding associated with lignin. Peak in the range 1710-1744 cm⁻¹ revealed -C-O-C ether bonds associated with lignin. Peak around 2850-3000 cm⁻¹ showed -C-H stretching associated with cellulose. The transmittance at about 3374 cm⁻¹, which related to O-H stretching of hydroxyl group in cellulose [9].

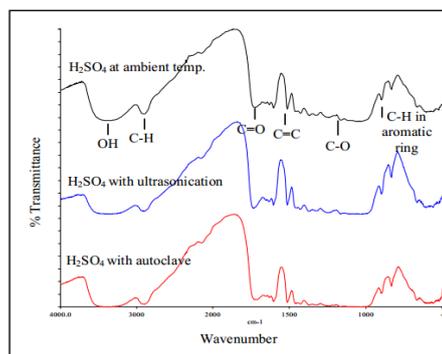


Fig. 1: FT-IR spectra of corn stalk by pretreated acid at ambient temperature, acid-ultrasonication and acid-autoclave.

The content of cellulose, hemicellulose and lignin of samples were shown in Fig.2. The results show that cellulose was the most abundance composition in all samples. Its comparatively high cellulose and low lignin content exhibited great potential on cellulosic ethanol production. It was remarkable observed in cellulose after pretreatment by acid-ultrasonication method (82.20% by weight) and acid-autoclave method (78.47 % by weight). It may be due to the application of ultrasonic irradiation and autoclave that produces intimate contact between the reactants resulting in increases reaction rates. The results of the determination of sugar yield are presented in Fig. 3. It was noticed that sugar yield of all pretreated sample were quite similar (30.51-32.94 mg/mL). It may be due to all pretreatment processes could alter or remove lignin led to increase the accessibility of acid to cellulose and decrease

the crystallinity of cellulose. The action mode of sulfuric acid is to solubilize hemicellulose and remain lignin and cellulose contact so that the digestibility of cellulose is enhanced. However, it required much time for decomposition of these compounds by using only dilute acid (1 day). Ultrasonication enhanced fermentable sugar release during acid hydrolysis of corn stalk, mainly due to reduction in particle size and better mixing. It can be described that when a frequency ultrasound wave propagates in a corn stalk medium, it produces cavitation and acoustic streaming. It generates large cavitation bubbles resulting in higher temperatures and pressures in the cavitation zone. The cavitation generates powerful hydro-mechanical shear forces in the bulk liquid, which disintegrate nearby particles by extreme shear forces. The main benefit of streaming in corn slurry processing is mixing, which facilitates the uniform distribution of ultrasound energy within the slurry mass, better mass transfer of acid, convection of the liquid and dissipation of any heating that occurs. As a result, ultrasound facilitates the disintegration of corn stalk granules, thereby exposing a much larger surface area to further acid hydrolysis [5].

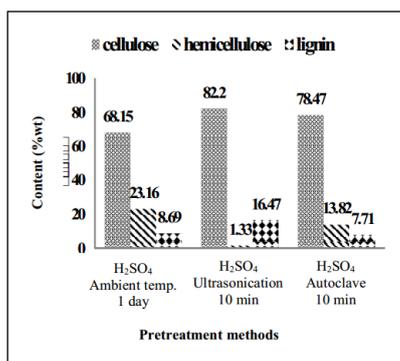


Fig. 2: Chemical composition content of corn stalk pretreated by acid at ambient temperature, acid-ultrasonication and acid-autoclave.

Acid-autoclave method could be removed a large part of the hemicellulose, causing an increase of cellulose. During stream pretreatment by autoclave, parts of the hemicellulose hydrolyze and form acids, which could catalyze the further hydrolysis of the hemicellulose. This process, in which the in situ formed acids catalyze the process itself, is called “auto-clave” stream pretreatment. High temperature and pressure in this process provide a faster rate of diffusion of acid molecule from solution to the structure of material. The role of the acid, is probably however not only to catalyze the solubilization of the hemicellulose, but also to catalyze the hydrolysis of the soluble hemicellulose oligomers resulting in sugar release [10]. Comparing of all methods, pretreatment using dilute acid combined with ultrasonication and autoclave method could accelerate the hydrolysis of sample and reduce the time required for proceed.

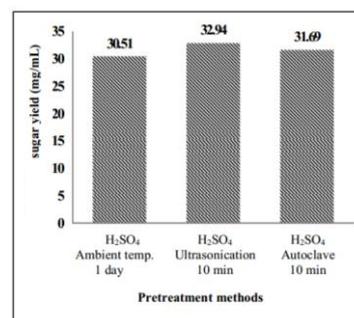


Fig. 3: Sugar yield of corn stalk pretreated by acid at ambient temperature, acid-ultrasonication and acid-autoclave.

3.2 Morphological features

SEM was used to study the morphological features and surface characteristics of materials obtained from different pretreatment methods. SEM micrographs of all pretreated samples in Fig.4 show that dilute sulfuric acid and physical treatment (ultrasonication and autoclave) disrupt the structure of fibers as present in their external surface. It was observed that pretreatment by dilute acid with ultrasonic and autoclave results in significant physical changes. The structure of lignocellulosic biomass was opened up and more sponge-like structures were observed, which can provide higher surface area for acid hydrolysis. In contrast, only dilute sulfuric acid pretreatment observed caused less change in structure.

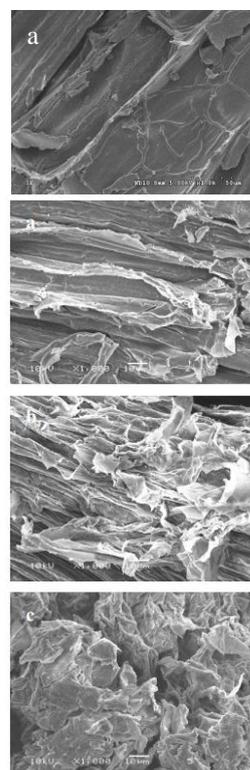


Fig. 4: SEM photographs of (a) corn stalk, (b) corn stalk pretreated by acid at ambient temperature, (c) acid-ultrasonication and (d) acid-autoclave.

4. Conclusion

The present investigation also shows that the dilute acid in combination with ultrasonication and autoclave pretreatments improved fermentable sugar yield with short processing time. However, there was no significant difference in sugar yield but the initial capital investment and operation cost of ultrasonication not cheap in scale up system. Therefore, dilute sulfuric acid in combination with autoclave pretreatment was found to be economically favorable, compared to those combined with ultrasonication in our studies.

5. Acknowledgement

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6. References

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Biography



Wimorath Tongpoothorn received her bachelor degree of Chemistry from Khon Kaen University in 1998. She received her master degree and doctoral degree in Chemistry from Khon Kaen University, Thailand in 2002 and 2012 respectively. She is currently a lecturer at the Faculty of Engineering, Rajamangala University of Technology Isan, Khon Kaen Campus. Her research interests include sustainable energy and adsorption of pollutant.



Kamonchanok Konglun received her bachelor degree of Chemistry from Rajamangala University of Technology Isan, Khon Kaen Campus, Thailand in 2013. She is currently a teacher at Paawhai Wittayakhom High School, Khon Kaen Province, Thailand.



Natnarin Seeto received her bachelor degree in Chemistry from Rajamangala University of Technology Isan, Khon Kaen Campus, Thailand in 2013. Currently, she's self-employed at Khon Kaen Province, Thailand.