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Process development for producing a food-grade glucose solution from rice straws



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ABSTRACT

In this paper, processes for producing a food-grade glucose solution through enzymatic hydrolysis of cellulose-rich solids obtained from rice straws are presented. The rice straws were pretreated by acid-catalyzed steam explosion, and the reaction efficiency, toxicity control, and process economic feasibility were studied. Mass transfer resistance to the hydrolysis reaction was reduced by grinding with glass beads. A higher glucose concentration could be obtained by feeding more cellulose in the hydrolysis reaction; however, this also resulted in the production of undesired byproducts. Thus, a soaking process for the cellulose solids in water was developed to effectively reduce the generation of byproducts in the hydrolysis reaction. The resulting food-grade glucose solution can provide 414 kilocalories per liter, and could be used during a food-shortage crisis in the future. The current production cost is estimated to be 0.82 USD · L⁻¹.

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1. Introduction

Agricultural waste is a widely available resource of lignocellulosic biomass, and has been considered an attractive material to produce alternative fuels and other biochemicals in recent decades. Lignocellulosic materials mainly comprise cellulose, hemicellulose, and lignin; notably, cellulose is a crystalline glucose polymer that can be used as a substrate for the production of bioethanol or valuable specialty chemicals *via* fermentation or chemical processes [1–8]. However, glucose is also an important food resource; it is not only fermented to produce edible yeast, a single-cell protein [9–11], but can also be directly used as food for energy supplementation. The concept of producing glucose as a food supplement from agricultural waste has been proposed in a few studies [11–14]; however, these studies have only focused on improving the efficiency of the cellulose hydrolysis reaction, such as optimizing the enzymatic hydrolysis condition [14] or applying a novel hydrolysis process to supercritical water systems [12]. To date, there has been no investigation on whether the concentrations of the byproducts (and their toxicity) in the resulting glucose solutions are within the safety limits, and if not, the ways to reduce them.

Growing concern that climate change may cause a food shortage in the future was the motivation for the present research. One global study [15] suggested that climate change can adversely impact maize and wheat production, resulting in a decrease in production of approximately 3.8% and 5.5%, respectively. Producing food from agricultural waste may

offer an alternative for overcoming shortage problems during a food crisis. Therefore, this paper presents processes for manufacturing a food-grade glucose solution through enzymatic hydrolysis of cellulose-rich solids produced from rice straws. The solids were obtained from a pilot plant in Taiwan, with a steam explosion process to produce bioethanol [16]. Specifically, rice straws were pretreated in a dilute sulfuric acid solution, following which they underwent steam explosion to destroy the crystalline structure. A mixture of cellulose-rich solid and xylose-rich liquid was produced. The feed used in this study was obtained from the cellulose-rich solids after filtration. For producing a high-quality food-grade glucose solution, a higher glucose concentration is preferred. However, this also produces undesired byproducts, such as formic acid, hydroxymethylfurfural (HMF), and furfural, which have an adverse effect on human health. Therefore, this study focused on increasing the hydrolysis efficiency to create a more highly concentrated glucose solution, control the solution toxicity, and present a preliminary economic evaluation of the process. The results elucidate the feasibility of producing a food-grade glucose solution from rice straw for future needs.

2. Experimental and Methods

2.1. Materials

Cellulose-rich solids produced from the processes reported previously [16] were used as the raw material for the hydrolysis reaction here. First, the rice straw was fed into a pulverizer and chopped into small pieces of approximately 1–2 cm. The resulting pieces were

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mixed with 1.3 wt% dilute sulfuric acid to form a solution with 50 wt% rice straw, which was then treated in a reactor under autogenous pressure at 110 °C for 4 h. Next, the rice straw was fed to a steam explosion vessel operating at 185 °C and 10 kg·cm⁻² pressure. An instant release of the pressure into the atmosphere caused the crystalline structure of the cellulose to collapse. After filtration, the cellulose-rich solids were obtained and used as the feed for the enzymatic hydrolysis reactor. The average moisture content of the cellulose-rich solids was 47 wt%, and the dry solids comprised 43% cellulose, 4% hemicellulose, and 53% lignin and ash.

2.2. Enzymatic hydrolysis reaction

Hydrolysis reactions were conducted in a 50-mmol·L⁻¹ acetate buffer solution (pH 4.8–5) at 50 °C for 24 h either in a 250-ml Erlenmeyer flask with a magnetic stirrer or in a glass batch reactor (6-cm inner diameter) with a mechanical propeller. Diagrams of the reactors are shown in the supplementary material (Fig. S1). The enzyme used for the reaction was a commercial cellulase (Novozyme Cellic CTec3) with an activity level of 15 FPU·g⁻¹. The glucose yield was calculated as follows:

$$\text{Glucose yield} = \left(\frac{\text{Glucose released in enzymatic hydrolysis}}{\text{Total monomers of cellulose in the feed}} \right) \times 100\%$$

2.3. Sugar analysis

The hydrolysates obtained from the enzymatic hydrolysis were first filtered with a 0.22-μm polyvinylidene fluoride syringe filter. The composition included glucose, formic acid, HMF, furfural, and sulfuric acid, and was analyzed using high-performance liquid chromatography, equipped with an ICsep ICE-ORH-801 column (from Transgenomic Technologies) and a refractive-index detector. The column was constantly eluted with 5 mmol·L⁻¹ H₂SO₄ at a flow rate of 0.6 ml·min⁻¹ at 35 °C.

2.4. Byproducts allowance in food-grade glucose solution

According to the U.S. Food and Drug Administration (U.S. FDA), the byproducts (formic acid, HMF, and furfural) in a glucose solution may induce slightly adverse effects on human health; however, they are also natural components of many foods and are used as food additives belonging to the Generally Recognized As Safe category. In particular, HMF is a natural ingredient of honey; however, ingesting more than 2 mg·kg⁻¹ body mass per day may be harmful [17]. Moreover, it is advisable that the formic acid intake limitation be within 8 mg·kg⁻¹ body mass per day [18] and that of furfural be within 54 mg·kg⁻¹ body mass per day [19]. Accordingly, a maximum of 480 mg of formic acid, 120 mg of HMF, and 3240 mg of furfural per day can be safely consumed for a person who weighs 60 kg. In this study, the use of a glucose solution as food was evaluated using these criteria.

2.5. Process design and economic evaluation

The proposed plant produces a food-grade glucose solution from rice straws, which consists of 33% cellulose, 19% hemicellulose, 3.2% arabinan, 19% lignin, and 26% ash. The acid-catalyzed steam explosion process was designed to generate cellulose-rich solids according to the process parameters from previous research [16]. Additionally, a soaking process for the cellulose solids and an enzymatic hydrolysis process to convert the cellulose into a food-grade glucose solution were designed according to the process parameters obtained in this research. The estimation was based on 7200 h of operation per year and the energy was supplied by igniting the rice straw and solid wastes from the plant, assuming that the average heat of combustion is 14000 kJ·kg⁻¹.

The total production cost of the food-grade glucose solution includes capital cost (e.g., installed equipment and offsite investments), variable operating costs (e.g., raw materials, utilities, consumables, waste disposal, and product transportation), and fixed operating costs (e.g., costs of labor, maintenance, taxes and insurance, and administrative support). Notably, the evaluation of the equipment costs was based on the information of Towler and Sinnott [20] and Sieder *et al.* [21]. Detailed calculations are shown in the supplementary material, and all of the information for these calculations is listed in Table 1.

Table 1
Economic evaluation of fixed and variable operating costs [22]

<i>Fixed operating cost</i>	
Operating labor	Averaged to be 2000 (USD per month) per engineer in Taiwan, 33 engineers total
Maintenance	5% of the total capital cost
Taxes and insurances	2% of the total capital cost
Administrative and support	65% of the costs of operating labor cost plus maintenance
<i>Variable operating cost</i>	
Rice straws	0.11 USD·kg ⁻¹ [23]
Process water	0.00038 USD·kg ^{-1a}
Sulfuric acid	0.07 USD·kg ^{-1b}
Acetic acid	0.53 USD·kg ^{-1b}
Sodium acetate	3.55 USD·kg ^{-1b}
Enzyme	50 USD·kg ^{-1c}
Product transportation	0.077 USD·L ⁻¹ of solution ^d
Waste treatment	0.0015 USD·kg ⁻¹ of waste water [20]

^a Price for industrial water from Taiwan Water Corporation.

^b Import price from Customs Administration, Ministry of Finance in Taiwan.

^c Market price in Taiwan from Trump Chemicals Corporation.

^d Assuming that the distance of the product transportation, which is roughly from village to city, is 200 km: 2 m³ of the product solution is loaded per truck, of which the transportation energy efficiency is 2.8 km·L⁻¹ of diesel.

The total annual cost (TAC) was calculated according to Eq. (1). Depreciation of equipment was assumed to be 7 years, and the production cost was calculated according to Eq. (2).

$$\text{TAC (USD} \cdot \text{a}^{-1}) = \text{Operating cost (USD} \cdot \text{a}^{-1}) + \frac{\text{Capital cost (USD)}}{\text{Depreciation year}} \quad (1)$$

$$\text{Production cost (USD} \cdot (\text{L product})^{-1}) = \frac{\text{TAC (USD} \cdot \text{a}^{-1})}{\text{Productivity (L product} \cdot \text{a}^{-1})} \quad (2)$$

3. Results and Discussion

3.1. Glucose yield in different mixing systems

First, the reproducibility of the enzymatic hydrolysis of cellulose-rich solids in a 250-ml Erlenmeyer flask with a magnetic stirrer on the bottom was examined under the same reaction conditions (1 g cellulose solid in 50 ml solution, pH = 5, enzyme loading = 15 FPU of Cellic CTec3·g⁻¹ cellulose, 50 °C, and 24 h) as those reported in the previous research. The resulting glucose yield was 70.0% ± 0.1%, compared with the previously reported yield of 70.4%–76.4% [16]. The same reaction in a 300-ml barrel-like (height, 11 cm height; bottom diameter, 6 cm) glass batch reactor with a 4-cm-diameter mechanical impeller (speed, 200 r·min⁻¹), located in the center and well above the reactor bottom, was also examined. Nevertheless, only 58.2% ± 1.6% of the glucose yield was obtained with this mechanical impeller.

A mechanical impeller is often used for mixing in a large-scale batch reactor, and it is critical to know why this process lowered the glucose yield substantially compared with that using a magnetic stirrer. Several

possibilities (e.g., the effect of impeller diameter and speed, or the height of the impeller from the bottom) were examined. It was determined that the variation of impeller diameter from 3 to 4 cm and of impeller speed from 200 to 600 $\text{r} \cdot \text{min}^{-1}$ had little effect on glucose yield. For example, when the impeller speed was increased to 600 $\text{r} \cdot \text{min}^{-1}$, the glucose yield was 60%, an increase of only approximately 2% from that with 200 $\text{r} \cdot \text{min}^{-1}$. Notably, when the impeller was placed lower to the reactor, the glucose yield increased to 64.8%. Nevertheless, this value was still substantially lower than that using the magnetic stirrer (70%). **Fig. 1** shows the sizes of solid residues after the hydrolysis reaction in different reactors. In particular, the residues from the reactor with the magnetic stirrer were smaller than those from the reactor with the mechanical impeller. This indicates that during the reaction, the bar of the magnetic stirrer located at the reactor bottom can grind the cellulose-rich solids to a smaller size, resulting in a decrease in the mass transfer resistance between the cellulose and the enzyme.

To stimulate a grinding function similar to that of the magnetic stirrer, 5-mm-diameter glass beads were added to the reactor to enhance the enzymatic hydrolysis reaction rate. As shown in **Fig. 2**, the yields with the glass beads were substantially higher than those without the glass beads. Additionally, **Fig. 3** illustrates the effect of the number of glass beads per area on the glucose yields after 24 h of reaction. Specifically, the yield increased from 58.2% (without beads) to 66.1% (with beads), indicating an improvement of 8.1% when an average of 0.5 beads $\cdot \text{cm}^{-2}$ were added. The yield can be increased further to reach slightly more than 70% (similar to the yield with the magnetic stirrer) by adding approximately 1 beads $\cdot \text{cm}^{-2}$; no obvious improvements within the experimental error could be obtained with more beads.

In short, there can be a considerable mass transfer resistance for the enzymatic hydrolysis reactions of cellulose-rich solids in a batch reactor with an impeller for mixing, although the acid-catalyzed steam explosion pretreatment was used to collapse the cellulose crystalline structure. The addition of glass beads in the reactor bottom can provide

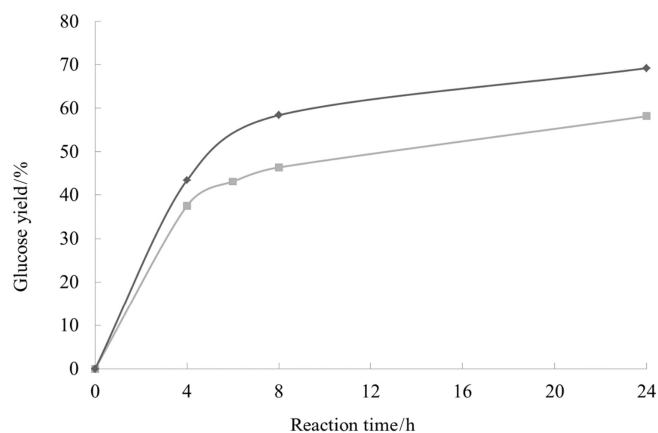


Fig. 2. Effect of glass beads on glucose yield during cellulose hydrolysis in the reactor with a mechanical impeller (cellulose solid loading, 1 $\text{g} \cdot (50 \text{ ml})^{-1}$; $\blacksquare$: no beads; $\blacklozenge$: an average of 1.1 beads $\cdot \text{cm}^{-2}$ of the reactor bottom).

a grinding effect on the cellulose-rich solids to reduce the mass transfer resistance, resulting in a higher glucose yield.

3.2. Production of glucose solutions with higher concentrations

The hydrolysis reaction results described in the preceding sections were obtained with a low initial concentration of 1 $\text{g} \cdot (50 \text{ ml})^{-1}$ of dry cellulose solids. The highest glucose concentration produced was only 6.8 $\text{g} \cdot \text{L}^{-1}$, which provided only 27 $\text{kcal} \cdot \text{L}^{-1}$ (based on 4 $\text{kcal} \cdot \text{g}^{-1}$ of glucose) (1 $\text{cal} = 4.1868 \text{ J}$); this value is not sufficient for human food supplements, thereby making a higher concentration yield necessary. Thus, higher loading of cellulose solids (i.e., 5 $\text{g} \cdot (50 \text{ ml})^{-1}$ and 10 $\text{g} \cdot (50 \text{ ml})^{-1}$) for the hydrolysis reactions is required. However, increasing the cellulose solids loading rendered the reaction solutions viscous and lowered the glucose yields. The final glucose concentrations

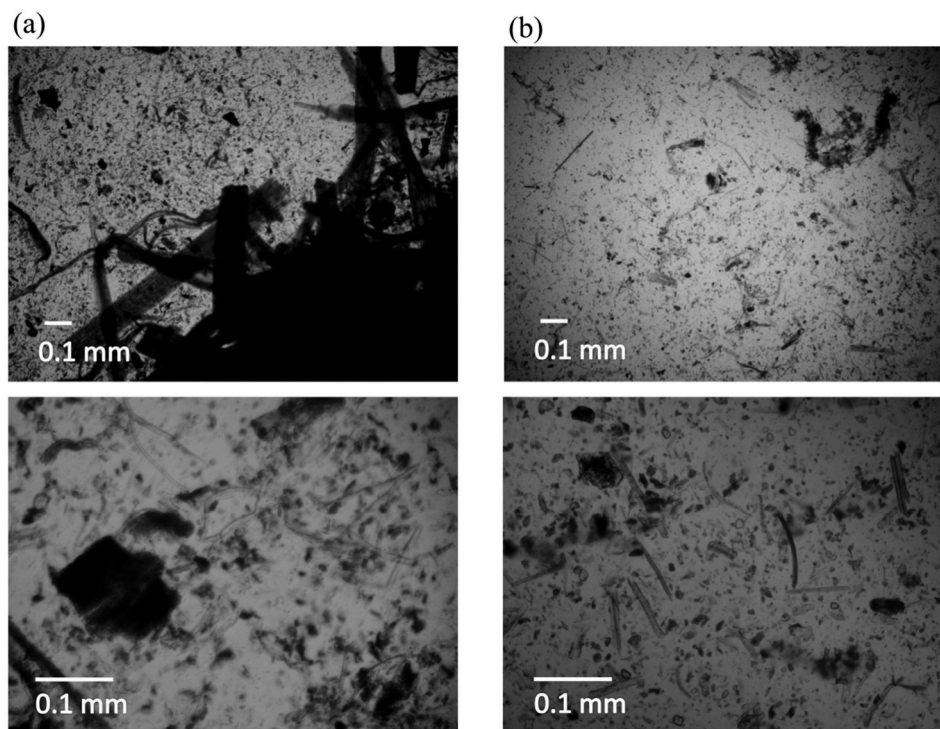


Fig. 1. Optical microscope images of the cellulose after enzymatic hydrolysis (a) in the glass batch reactor with a mechanical impeller, and (b) in the Erlenmeyer flask with a magnetic stirrer.

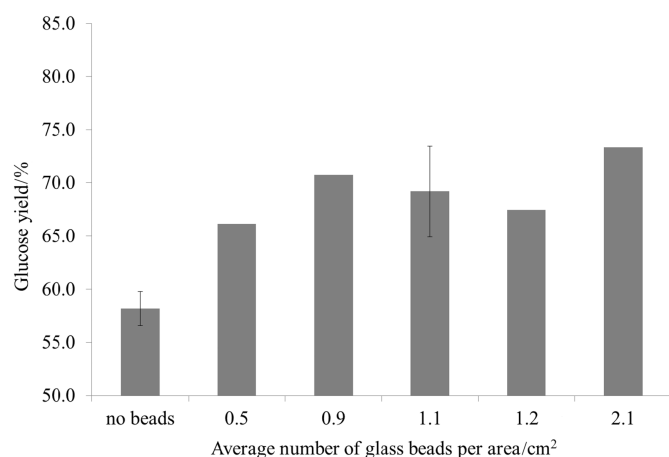


Fig. 3. Effects of the average number of beads $\cdot \text{cm}^{-2}$ of the reaction bottom on glucose yield (cellulose solid loading, $1 \text{ g} \cdot (50 \text{ ml})^{-1}$; reaction time, 24 h; reactor height, 11 cm height; reactor diameter, 6 cm).

can be increased as shown in **Table 2**. The glucose concentration increased from 6.8 to $33.2 \text{ g} \cdot \text{L}^{-1}$, slightly less than five times, when the initial cellulose loading was increased from $1 \text{ g} \cdot (50 \text{ ml})^{-1}$ to $5 \text{ g} \cdot (50 \text{ ml})^{-1}$. Moreover, the concentration could be increased to $53.1 \text{ g} \cdot \text{L}^{-1}$ (considerably less than ten times) when the initial cellulose loading was further increased to $10 \text{ g} \cdot (50 \text{ ml})^{-1}$. The calories of the glucose solutions with the two higher cellulose loadings were 133 and $212 \text{ kcal} \cdot \text{L}^{-1}$, respectively.

However, more undesired byproducts (*i.e.*, formic acid, HMF, and furfural) were also produced when cellulose loading was increased (**Table 2**). For example, when the cellulose feed was increased from $1 \text{ g} \cdot (50 \text{ ml})^{-1}$ to $10 \text{ g} \cdot (50 \text{ ml})^{-1}$, the HMF concentration after the hydrolysis reaction increased from 13 to $130 \text{ mg} \cdot \text{L}^{-1}$. Considering the maximum allowances of 120 mg of HMF per day, a person who weighs 60 kg cannot consume more than 1 L of this solution daily. This implies that only approximately 212 kcal can be obtained from the solution, which is considerably less than a person's daily nutritional requirement (*i.e.*, 1170 kcal). An increase in cellulose loading to achieve a more highly concentrated glucose solution would not be useful for food supplementing unless the amount of undesired byproducts can meet the toxicity requirement.

3.3. Soaking cellulose solid in water to reduce undesired byproducts

HMF can be produced from the dehydration reaction of glucose. Formic acid is a byproduct of the production of levulinic acid from the

hydrolysis reaction of HMF. Additionally, furfural is usually produced from the dehydration reaction of xylose, which is produced from the hydrolysis reaction of hemicellulose (4%) remaining in cellulose-rich solids. All of these reactions can be catalyzed using an acid. However, some undesired byproducts and acid remain in cellulose-rich solids collected from the acid-catalyzed steam explosion process. The more cellulose-rich solids are fed in the reaction, the more undesired products are produced and the more acid is released into the solution. The acid can inevitably catalyze the generation of the undesired products in the enzymatic hydrolysis reaction of cellulose. In this study, the soaking process was employed to remove the undesired byproducts and the acid from the cellulose-rich solids prior to the enzymatic hydrolysis reaction. This was attempted by soaking 10 g of dry cellulose-rich solids into 50 or 100 ml of water for 10 min, following which the dissolution of the undesired byproducts and the acid from the solid was expected. Fewer byproducts may be left in the solid when more water is used. The soaking process was conducted without any mixing. Additionally, no grinding effect can occur on the cellulose-rich solids; thus, only the effect of the acid and byproduct removal on the later enzymatic hydrolysis reaction was investigated.

Table 3 presents a list of the effects of water amount for soaking cellulose-rich solids (for 10 min) on the production of glucose and byproducts from (10 g dry cellulose-rich solid per 50 ml feed for) enzymatic hydrolysis reaction. The concentrations of all of the undesired byproducts (*i.e.*, HMF, formic acid, and furfural) decreased with an increase in the amount of soaking water. Specifically, when the solids were soaked in 10 ml of water per gram of solid, the resulting concentrations of formic acid, HMF, and furfural in the liquid produced thereafter were reduced to 128, 36, and $290 \text{ mg} \cdot \text{L}^{-1}$, respectively; without the soaking process, these concentrations were 361, 130, and $443 \text{ mg} \cdot \text{L}^{-1}$, respectively. Moreover, the glucose concentration after soaking increased substantially to $62.1 \text{ g} \cdot \text{L}^{-1}$ compared with only $53.1 \text{ g} \cdot \text{L}^{-1}$ without soaking. These results can be verified and explained by the amount of acid released during the soaking process, as shown in the data listed in **Table 4**. This implies that when more soaking water was used, more acid was released, resulting in less acid remaining for catalyzing the production of undesired products in the hydrolysis reaction process. Less acid also corresponded to a smaller amount of glucose being converted into HMF and other byproducts; thus, a higher concentration of glucose can remain, resulting in a higher yield. Furthermore, less acid can reduce the catalysis of the hydrolysis reaction of xylose, resulting in a reduced concentration of furfural (**Table 3**).

According to the food regulations for a person weighing 60 kg, the daily maximum allowances are no more than 480 mg of formic acid, 120 mg of HMF, and 3240 mg of furfural. As indicated, the glucose solution prepared from the enzymatic hydrolysis of cellulose-rich solid that was pretreated for 10 min with 10 ml of soaking water per gram of solid contains formic acid, HMF, and furfural at concentrations of

Table 2

Glucose and byproduct concentrations produced from various cellulose loadings (with an average of 1.1 beads per cm^2 on the reactor bottom) after 24 h

Cellulose feed concentration/ $\text{g} \cdot (50 \text{ ml})^{-1}$	Glucose yield/%	Glucose/ $\text{g} \cdot \text{L}^{-1}$	Formic acid/ $\text{mg} \cdot \text{L}^{-1}$	HMF/ $\text{mg} \cdot \text{L}^{-1}$	Furfural/ $\text{mg} \cdot \text{L}^{-1}$
1	69.2	6.8	34	13	55
5	67.1	33.2	184	58	291
10	53.2	53.1	361	130	443

Table 3

Effect of soaking-water amount on the production of glucose and byproducts from the enzymatic hydrolysis reaction (soaking time, 10 min; concentration of dry cellulose-rich solid, $10 \text{ g} \cdot (50 \text{ ml})^{-1}$; hydrolysis reaction time, 24 h; average number of glass beads per cm^2 area of reactor bottom, 1.1)

Soaking water (ml) per g of cellulose solid	Glucose yield/%	Glucose/ $\text{g} \cdot \text{L}^{-1}$	Formic acid/ $\text{mg} \cdot \text{L}^{-1}$	HMF/ $\text{mg} \cdot \text{L}^{-1}$	Furfural/ $\text{mg} \cdot \text{L}^{-1}$
0	53.2	53.1	361	130	443
5	56.0	53.6	138	50	292
10	62.1	62.1	128	36	290

Table 4

Amount of acid and byproducts dissolved in the soaking water [soaking time, 10 min; concentration of dry cellulose-rich solid, 10 g·(50 ml)⁻¹]

Soaking water per g of cellulose solid/ml	Sulfuric acid/mmol	Formic acid/mg	HMF/mg	Furfural/mg
0	–	–	–	–
5	2.1	9.9	3.9	11.1
10	4.6	10.4	3.9	13.7

128, 36, and 290 mg·L⁻¹, respectively. If a person consumes 2 L of the solution daily, only 256, 72, and 580 mg per day of formic acid, HMF, and furfural, respectively, are consumed; these values are lower than the maximum respective allowances, indicating that the concentrations of all the byproducts in the glucose solution are within the safety limits of food regulation. Moreover, a person can obtain 496 kcal from drinking 2 L of this solution per day, which is approximately 42% of the daily requirement (i.e., 1170 kcal). Although this intake is not sufficient to entirely meet the daily requirement of a person weighing 60 kg, the process for converting rice straws to this drinkable glucose solution can partially help overcome the problem of food shortages during a food crisis in the future.

To obtain a glucose solution with even more calories, further effort to remove additional acid and undesired products was made by increasing the soaking time for the cellulose-rich solid, from 10 to 30 min. After the enzymatic hydrolysis reaction with an initial cellulose-rich solid loading of 10 g·(50 ml)⁻¹, the concentrations of formic acid, HMF, and furfural were reduced further to 98, 28, and 251 mg·L⁻¹, respectively. However, the glucose concentration also unexpectedly reduced to 49.4 g·L⁻¹ (i.e., only providing 197 kcal·L⁻¹), which was even lower than that from the solid feed without any soaking in water. This may indicate a considerable dissolution and loss of cellulose from the cellulose-rich solid during the longer soaking process. The experimental data listed in **Table 5** show that the mass of the solid feedstock after soaking in water for 30 min was substantially lower (by 0.7 g) than that after soaking for 10 min. The decrease of the mass of glucose by (0.6 ± 0.1) g produced from the hydrolysis reaction corresponds satisfactorily to the lower mass of the cellulose solid feedstock for the reaction.

Table 5

Effect of soaking time on the mass of cellulose-rich-solid feeds and the amount of glucose produced in the hydrolysis reaction (soaking water amount per g of cellulose solid, 10 ml)

Soaking time/min	Feedstock for hydrolysis reaction ^a /g	Glucose amount from the hydrolysis reaction ^b /g
10	21.6	3.1
30	20.9	2.5 ± 0.1 ^c

^a Mass of the cellulose solid after soaking process, which is used as the feed for the later hydrolysis reaction (the dry cellulose used before soaking is 10 g).

^b Each value is obtained from the glucose concentration of the resulting solution multiplied by the volume of the solution (50 ml).

^c Value is the average of three replicates.

3.4. Effect of enzyme concentration on glucose production in the hydrolysis reaction

To optimize the yield and concentration of glucose produced from the hydrolysis reaction, the effect of the amount of enzyme used for the reaction was investigated. The experimental results listed in **Table 6** indicate that the glucose concentration can increase substantially from 49.0 to 62.1 g·L⁻¹ (i.e., a 13% increase in glucose yield) by increasing the enzyme addition from 7.5 to 15 FPU·g⁻¹ cellulose. However, when the enzyme addition was increased to 30 FPU·g⁻¹

Table 6

Effect of enzyme loading on glucose production from the enzymatic hydrolysis reaction (soaking water amount per g of cellulose solid, 10 ml; soaking time, 10 min; concentration of dry cellulose-rich solid, 10 g·(50 ml)⁻¹; hydrolysis reaction time, 24 h; average number of glass beads per cm² area of reactor bottom, 1.1)

Enzyme loading /FPU·(g cellulose) ⁻¹	Glucose yield /%	Glucose concentration /g·L ⁻¹
7.5	49.1	49.0
15	62.1	62.1
30	66.2	66.1
45	69.7	69.8

cellulose, the glucose yield increased by only approximately 3%. This suggests that most of the cellulose solid surface was occupied by the adsorbed enzyme when the added amount was increased (i.e., higher than 15 FPU·g⁻¹ cellulose). Notably, the unadsorbed enzyme cannot contact the solid to catalyze the hydrolysis reactions. Because the use of the enzyme is the main cost of the whole production process, in this study, a suitable amount of enzyme addition for glucose production was determined to be 15 FPU·g⁻¹ cellulose.

3.5. Economic evaluation for food-grade glucose solution

A process for producing a food-grade glucose solution from rice straws was evaluated based on the biomass pretreatment processes of acid-catalyzed steam explosion [16], and soaking process and enzymatic hydrolysis process developed in this research. The objective was to produce a solution with a glucose concentration of 62.1 g·L⁻¹, which can provide 248 kcal·L⁻¹ for human consumption. The overall flow of the production processes is illustrated in **Fig. 4**. They are carried out by that after the steam explosion process and the filtration process, the obtained cellulose-rich solids are soaked in fresh water that weighs 10 times the amount of the solid for 10 min. This soaking process leaches the remaining acid and byproducts out of the solid. After further filtration, the cellulose-rich solids are fed into an enzymatic hydrolysis reactor (operating conditions: cellulose-rich solid loading, 10 g·(50 ml)⁻¹; solution pH, 5; enzyme loading, 15 FPU of Cellic CTec3·g⁻¹ cellulose; temperature, 50 °C; time, 24 h). Subsequently, the obtained glucose solution is treated *via* pasteurization at 90 °C, which kills microbes. Finally, a food-grade glucose solution with a glucose concentration of 62.1 g·L⁻¹ is obtained.

The economic evaluation of the glucose solution, in terms of capital cost, variable operating costs, and fixed operating costs, is listed in **Tables 7** and **8**. The capital cost was determined to be 9.9 million USD·a⁻¹, whereas the variable and fixed operating costs were determined to be 13.1 and 2.0 million USD·a⁻¹, respectively. Additionally, the TAC is calculated using Eq. (1), and was determined to be 16.5 million USD·a⁻¹. In this study, annual production of the solution from a plant processing 1500 kg of rice straw feedstock per hour (7200 operating hours per year) was set at 33.5 million liters. Thus, the production cost of a food-grade glucose solution with 248 kcal·L⁻¹ was calculated to be 0.50 USD·L⁻¹ according to Eq. (2). Based on the mass of the glucose in the solution, the production cost was estimated to be 8.16 USD·kg⁻¹ of glucose, which is considerably higher than the current price of glucose (0.77 USD·kg⁻¹, the average import price to Taiwan in 2015).

Moreover, the cost of the enzymatic hydrolysis reactor contributes to approximately 40% of the overall capital cost. The cost of the enzyme is the most expensive variable operating cost; indeed, because of the high price of commercial enzymes (50 USD·kg⁻¹), the enzyme cost is approximately 56% of the TAC. However, if cheaper enzymes that can be produced using more economical processes are available, the cost of the food-grade glucose solution can be lowered. For example, **Fig. 5** reveals that if the cost of commercial enzymes decreases to one-tenth of the current price, the cost of glucose can be decreased by almost 50% (i.e., to 4.32 USD·kg⁻¹). Notably, this is still much higher than the

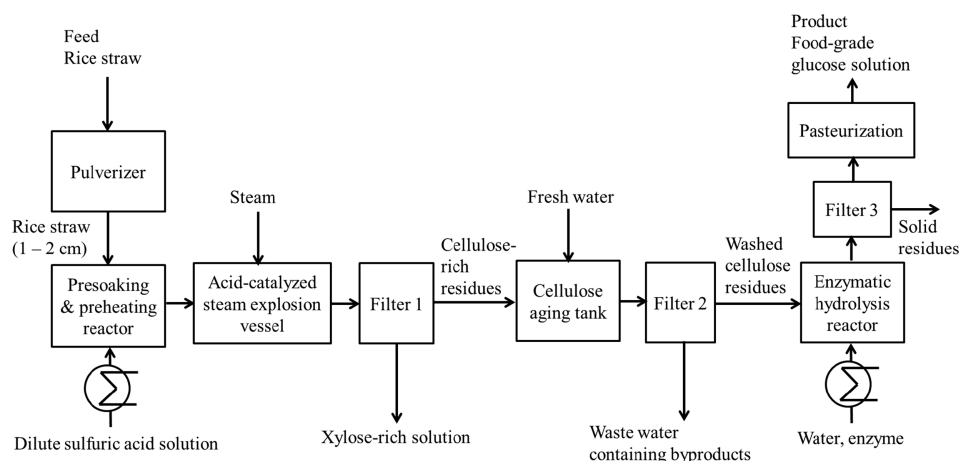


Fig. 4. Schematic flow diagram of the food-grade glucose solution production process.

Table 7

Estimated operating costs for producing the food-grade glucose solution

Variable operating cost		
	Quantity	Cost/thousand USD · a ⁻¹
Rice straw for feedstock	1500.0 kg · h ⁻¹	1188
Rice straw for energy supply ^a	863.7 kg · h ⁻¹	732
Electricity	3.66 kW	2
Process water	25876.3 kg · h ⁻¹	71
Sulfuric acid	24.3 kg · h ⁻¹	12
Acetic acid	7.0 kg · h ⁻¹	27
Sodium acetate	9.5 kg · h ⁻¹	244
Enzyme	23.9 kg · h ⁻¹	8612
Waste water treatment	13071.1 kg · h ⁻¹	141
Product transportation	4647.6 L · h ⁻¹	2565
Residues for energy supply	670.9 kg · h ⁻¹	–531
Total		13064
Fixed operating cost		
		Cost/thousand USD · a ⁻¹
Operating labor		792
Maintenance		357
Taxes and insurances		143
Administrative and support		747
Total		2039

^a Energy supply for the steam explosion of rice straw, heating, and product pasteurization.

Table 8

Estimated capital cost for producing the food-grade glucose solution

Equipment	Size	Material ^f	Cost/thousand USD
Pulverizer	1500 kg · h ⁻¹	CS	52
Heater for preheating	3.7 m ² , ^a	SS	24
Heater for enzymatic hydrolysis	1.4 m ² , ^a	SS	11
Presoaking & preheating reactor	16.7 m ³ , ^b	SS	738
Steam explosion vessel	9503 kg, ^c	SS	809
Filter 1	18.6 m ² , ^d	SS	332
Tank for soaking process	178.8 m ³ , ^e	SS	238
Filter 2	16.6 m ² , ^d	SS	499
Enzymatic hydrolysis reactor	2 reactors of 84.0 m ³ , ^b	SS	2647
Filter 3	27.6 m ² , ^d	SS	395
Boiler for steam generation	4089 kg · h ⁻¹ steam	SS	321
Equipment for pasteurization	59.9 m ² , ^a	SS	348
Tank for product storage	137.8 m ³ , ^e	SS	207
Total installed equipment cost			6621
Capital cost			9931

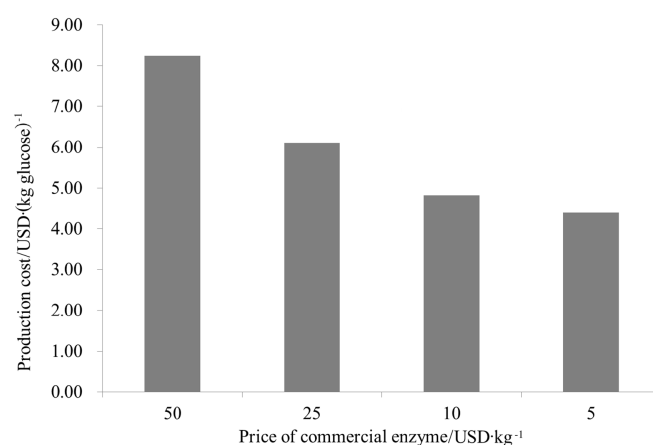
^a Heat transfer area of heat exchange.^b Volume of reactor.^c Mass of pressure vessel.^d Filtration area of filter.^e Volume of tank.^f Materials of equipment. Carbon steel (CS); Stainless steel (SS).

Fig. 5. Effect of enzyme price on the production costs of food-grade glucose solutions (62.1 g of glucose per liter of solution).

current price of glucose. Nevertheless, the amount of the food-grade glucose solution produced from the plant can fulfill the daily nutritional requirement of approximately 45000 people who consume 2 L of the glucose solution per day (496 kcal · d⁻¹). If the total amount of rice straw in Taiwan, approximately 1.5 million tons of rice straw produced every year, can be collected for producing the glucose solution, the daily nutritional requirement of approximately 5 million people during a food shortage can be fulfilled.

An evaporation process can be used to produce a more concentrated food-grade glucose solution, resulting in more calories in the solution. However, to avoid the generation of undesired byproducts (*i.e.*, HMF, formic acid, and furfural), the evaporation process must be performed under vacuum at a low temperature (*e.g.*, at 50 °C). On the basis of the daily intake of HMF (120 mg) and water (2 L) for a person weighing 60 kg, the original solution with a glucose concentration of 62.1 g · L⁻¹ can be concentrated to 103.5 g glucose · L⁻¹ (414 kcal · L⁻¹), and can contain 213, 60, and 480 mg · L⁻¹ of formic acid, HMF, and furfural, respectively. In other words, a person who consumes 2 L of the solution per day will be within the toxicity allowance, and can obtain 818 kcal, which constitutes up to 70% of the daily nutritional requirement (*i.e.*, 1170 kcal). A comparison of the economic evaluations for the original and concentrated food-grade glucose solutions are shown in Table 9. Notably, although concentrating the glucose solution through evaporation increases the production cost, the transportation cost can decrease from 15.5% to 9.4% of the TAC. Therefore, there is no increase in the TAC per gram of glucose produced for creating a concentrated glucose solution. It was determined that 20.1 million liters of the

Table 9

Estimated production costs for the original and concentrated food-grade glucose solutions

	Original solution	Concentrated solution
Enzyme hydrolysis	55.9% ^e	56.6% ^e
Vacuum evaporation of product	–	3.2% ^e
Product transportation	15.5% ^e	9.4% ^e
Steam explosion	5.3% ^e	5.5% ^e
Feedstock and chemicals	9.2% ^e	9.2% ^e
Other cost ^a	1.9% ^e	1.6% ^e
Fixed operating cost ^b	12.3% ^e	14.5% ^e
Total annual cost (TAC)	16.5 million USD·a ⁻¹	16.2 million USD·a ⁻¹
Productivity	33.5 million L·a ⁻¹	20.1 million L·a ⁻¹
Production cost ^c	8.16 USD·kg ⁻¹	8.05 USD·kg ⁻¹
Production cost ^d	0.49 USD·L ⁻¹	0.81 USD·L ⁻¹

^a Cost includes product storage, product pasteurization, and waste water treatment.^b Cost includes operating labor, maintenance, taxes and insurance, and administration and support.^c Production cost was based on the mass of the glucose contained in the product solution.^d Production cost was based on the volume of the food-grade glucose solution.^e Percentage of the total annual cost (TAC).

concentrated glucose solution can be produced annually in the plant, which would fulfill approximately 70% of the daily nutritional requirement of 27000 people. The production cost is approximately 0.82 USD·L⁻¹.

Although the production cost is expensive, the process developed in this study can produce a substantial amount of food-grade glucose solution during a food crisis. If food demand and prices increase in the future, this process has the potential to serve as an alternative way to overcome the food crisis.

4. Conclusions

This study demonstrated the feasibility of using rice straw to produce a food-grade glucose solution. The resulting solution contained 103.5 g·L⁻¹ of glucose (414 kcal·L⁻¹), which can be supplied for human needs in the future. If a plant processes 1500 kg of rice straw feedstock per hour (7200 operating hours per year), 20.1 million liters of the glucose solution could be produced annually, which can satisfy 70% of the daily caloric needs of 27000 people. The production cost of the solution is approximately 0.82 USD·L⁻¹, mainly because of the cost of the enzyme used in the hydrolysis reaction. Although the production cost is higher than the current price of glucose, a large amount of the food-grade glucose solution can be produced and supplied during food crises in the future.

A considerable mass transfer resistance was observed during the enzymatic hydrolysis reaction of cellulose-rich solids in an impeller-stirred batch reactor. This resistance can be reduced by adding glass beads in the reactor to help ground the solid during the reaction. Although an increase in the production of glucose increases the production of undesired byproducts, owing to the feeding of more cellulose, a soaking process for the cellulose-rich solids can effectively reduce the generation of undesired byproducts; this enables the food-grade glucose solution to remain within the regulatory limits. It was determined that the enzyme addition of 15 FPU·g⁻¹ cellulose is close to an optimum amount for glucose production.

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Supplementary Material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.cjche.2017.06.004>.

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