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Xylose Recovery from Pineapple Peel Biomass by Mild Acid Hydrolysis

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Waste disposal issue is among of highly concerned issue all over the world. In Malaysia, this waste usually ends up being in landfills. This is not any exception especially in agriculture and manufacturing industry whose has to deal with many-by-products after a production. Thus, in this study focuses on by-product from canning and beverage industry which is pineapple peel for its xylose recovery. The aim of this recovery is to provide cost effective means of producing high-end product such xylitol. In this study, crucial parameter of mild hydrolysis was optimized by using One-Factor at Time (OFAT) method. Batch hydrolysis was carried out with the following parameters: acid concentration (0.5–7%), residence time (5–50 min), and temperature (80–130 ^{0}C). As a result, the highest xylose concentration obtains around 20 g/L under the condition of 5 % nitric acid concentration, 105°C for 20 min residence time. The result showed this method can yield up to 85 % of actual xylose concentration from the hemicellulose degradation. Altogether, the finding of this study is beneficial to the pineapple industry, especially in light of recent discussion in terms of waste disposal issue and its impact on greenhouse gas emission.

1. Introduction

Malaysia, one of the leading agricultural producers in Southeast Asia, produces 336x10^3 t of pineapple annually (Hamzah et al., 2021). Taking into account of the fact that due to variety factors, cultivation of pineapple trees is expected to grow rapidly in Malaysia, particularly the insistence of the canning and beverage industries. However, this industry is facing with waste disposal issue of the by-products from the manufacturing. These by-products like pineapple peel and its core often thrown away into the landfills which contributes to the greenhouse effect. Consequently, this issue just could be averted by turning these by-products into a high value-added product, which not only increases capital earnings but also reduces the volume of waste in landfills. Thus, it is interesting to investigate the energy potential of these by-products from the pineapple industry which is coherent to the current European policies. The energy potential could promote circular economy in terms of the recycle and reuse of various by-products which also can create a high value-added product namely, xylitol. Currently, the demand of xylitol in food industry, confectionary, cosmetic, pharmaceutical and others contributes to 40 % of xylitol production in Malaysia. It is expected that in the near future, the use of xylitol will increase to 50 % of total market value. In 2015, xylitol market estimated to grow by CAGR of 2.9 % to reach USD 1.1x10^9 by 2025 (IndustryARC, 2022).

Current xylitol manufacture utilizes a chemical method called catalytic hydrogenation despite their high manufacturing cost. To counter this, numerous scientists, agree that making xylitol using biotechnological means is the most efficient and cost-effective option (Umai et al., 2022). Xylose is used in both processes, where this xylose commonly extracted from the lignocellulosic biomass provides a greener sustainable source compared to its synthetic equivalents. For example, this biomass has been explored for the xylose recovery soybean hull (Tadimeti et al., 2022), sugarcane bagasse (West, 2021), corn stover (Zhang et al., 2011) etc. It

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should be noted that different lignocellulosic biomass composed of different constituents which can be contributed to the xylose recovery. Thus, the purpose of this study is to evaluate the ability of lignocellulosic biomass of pineapple peel to produce sustainable fermentable sugar of xylose in order to meet the production needs of the xylitol manufacturing industry while improving the disposal efficiency of lignocellulosic biomass.

2. Theory

Pineapple peel (PP) is one of the lignocellulosic biomasses shown in Figure 1 that is constituted fibrous and hard-to-break-apart cellulose, hemicellulose, and lignin (Solarte-Toro et al., 2019). PP is a lignocellulosic biomass consists of around 22–45 % dry matter cellulose, 21–75 % dry matter hemicellulose, and 2–14 % dry matter lignin (Sukkaew et al., 2017). This makes PP an excellent resource for the sustainable fermentable sugar of xylose. The majority of sugar in this biomass is extracted by degrading cellulose and hemicellulose. Therefore, an efficient pretreatment is necessary to overcome the rigid structure of lignocellulose and allow easy access of cellulose and hemicellulose by increasing the surface area of the biomass.

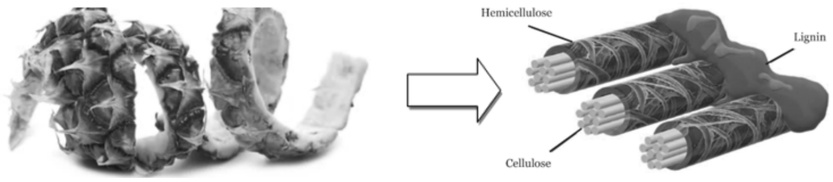

Figure 1: Pineapple peel lignocellulosic biomass constituent (Anukam and Berghel, 2020)

There are three main pretreatments of this breakdown process; physical, chemical and biological. Numerous research has utilised the traditional acid hydrolysis through the usage of sulfuric acid. Nevertheless, this conventional sulfuric acid hydrolysis is a powerful acid that is undesirable as it generates several inhibitor byproducts. Therefore, it is preferable to employ a moderate acid hydrolysis using nitric acid that can hydrolyze at a quick pace while concurrently decreasing the inhibitor concentration (Manaf et al., 2018). Rafiqul & Sakinah(2012) revealed that this acid hydrolysis pretreatment process is influenced by three critical parameters: acid concentration, temperature, and residence time. These characteristics vary depending on the compositional nature of the biomass utilized. Thus, the objective of this research is to assess the hemicellulose and cellulose degradation which leads to the production of a high fermentable sugar. The high fermentable sugar is extracted from the pineapple peel. Consequently, the degradation process is achieved through varying crucial parameters of the acid hydrolysis. Hence, this research aims to optimize this hydrolysis condition for a high recovery xylose sugar from this specifically biomass.

3. Methods

3.1 Raw material

The pineapple peel was supplied and collected in Kulim. The fresh pineapple peel was chopped into tiny pieces. The pineapple peels were exposed to the sun for five days to remove existing moisture in it. Afterwards, the biomass was ground to a particle size of 2 mm using a cutting mill (Model: Pulverisette 19, Fritsch, Germany). The sample was then placed in an airtight container and kept at room temperature for future use.

3.1 Biomass compositional analysis

National Renewable Energy Laboratory (NREL) Analytical Procedure was used to analyse the elements of pineapple peel. The primary focus of the components is on structural carbohydrates, total extractives, and lignin. In this technique, the sample's extractives were first eliminated entirely to prevent interference. This was accomplished through 3 h of water extraction followed by 3 h of 95% ethanol extraction using the Accelerated Solvent Extraction ASE 350 (ASE-Dionex, Sunnyvale, CA, USA) (Manaf et al., 2018). As a result, the processes produced three main samples: water extraction, ethanol extraction, and extractive free PP biomass as shown in Figure 2.
Water-extract and extract-free PP biomass samples were subjected to acid hydrolysis. High-performance liquid chromatography (HPLC) was used to assess the sugar polysaccharide from the water extract, hydrolysate of the water extract, and extract-free PP biomass. The total sugar polysaccharide from these three samples were quantified as cellulose and hemicellulose. Then, the extractive-free PP biomass hydrolysate was filtered, dried, and recorded as acid-insoluble lignin.

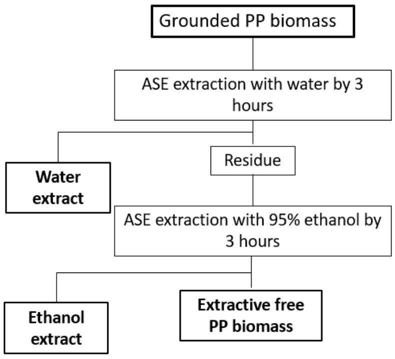

Figure 2: Accelerated Solvent Extraction (ASE) extraction procedures of pineapple peel (PP) for water extract, ethanol extract and extractive free biomass samples

3.3 Hydrolysis condition

For the hydrolysis, nitric acid was used. Hydrolysis was performed at a 10:1 (mL: g) liquid to solid ratio by suspending 10 mL of nitric acid in 1 g of the dried biomass with moisture content less than 10 % (Luthfi et al., 2016). This hydrolysis was taken place in 50 ml screw capped Erlenmeyer flask. The hydrolyzed liquid was stored in a Duran bottle for later analysis. The solid waste was washed with water, thereafter dried in an oven at 45 °C for 24 h, weighed and analyzed. Lastly, the liquid hydrolysate was analyzed using HPLC to assess various sugars in g/L.

3.4 OFAT hydrolysis run

OFAT method were used to determine the optimum range of the crucial hydrolysis parameters which are concentration of acid, temperature and residence time. The parameters were chosen based on the range of previous research (Manaf et al., 2018). As far as the literature can be found, the range found for those parameters are 1 –7 % for acid concentration, 105 – 130 °C for temperature and 5 – 40 min for residence time (Manaf et al., 2018). OFAT hydrolysis commenced of three stages hydrolysis. In the first stage, the hydrolysis was taken place by varying the acid concentrations while maintaining the temperature and residence time at 130 °C for 20 min as control. In the next stage, the best acid concentration from the stage 1 was used for this hydrolysis while varying the temperature for 20 min. For the last stage, using the best acid concentration and temperature from stage 1 and stage 2, this hydrolysis was run with various residence time. The best acid concentration and the best temperature were chosen based on its ability to produce the highest sugar concentration. The overview OFAT parameter varied can be seen in Table 1. The performance of the acid hydrolysis pre-treatment can be determined by calculating the xylose recovery percentage using equation 1.

Table 1: Overview OFAT hydrolysis run stages

Stage	Nitric acid concentration (%)	Temperature (°C)	Residence time (min)
1	1 – 7	130 (Manaf et al., 2018)	20 (Manaf et al., 2018)
2	Determined from stage 1	105 – 130	
3	Determined from stage 1	Determined from stage 2	10 – 60

The xylose recovery after the mild acid hydrolysis pre-treatment was calculated as follows:

$$Xylose\ recovery\ (\%) = \frac{Xylose\ on\ pretreated\ hydrolysate\ \times 0.88}{Hemicellulose\ content\ in\ raw\ biomass} \times 100\% \quad (1)$$

Where 0.88 is the conversion factor of xylose to its equivalent hemicellulose.

3.5 Analytical method

Using High Performance Liquid Chromatography, HPLC (UltiMate 3000 LC system, Dionex, Sunnyvale, CA) with a refractive index (RI) detector, the concentrations of sugar monomers and acetic acid resulting from hydrolysis were measured (RefractoMax 520, ERC, Germany). The sample was passed through a Rezex ROA-Organic acid column (300 mm 7.8 mm; Phenomenex, USA) and a guard column (50 mm 7.8 mm; Phenomenex, USA) at a temperature of 60 °C. The mobile phase, which consisted of 5 mM sulfuric acid, was eluted isocratically at 0.6 mL/min.

Using HPLC, the concentrations of furfural and HMF were likewise quantified, however samples were conducted under different column and mobile phase conditions. The sample was processed on a Gemini C-18 column (Phenomenex, USA). The temperature of the column was controlled at 40 °C. The mobile phase was 20mM sulphuric acid:acetonitrile (1:10) at a flow rate of 0.8 mL/min.

4. Result and discussion

Composition of pineapple peel

The pineapple peel was characterized using the NREL technique. The pineapple peel average composition consisted of 42.9 % cellulose, 20.7 % hemicelluloses, 9.4 % lignin, 2.7 % ash, 4.6 % crude protein and 18.8 % total extractives as shown in Table 2. The compositions from various sources were also presented and compared, Pardo et al. (2014) result has the most similarities to this study compared to other studies. This variation of the result was due to several factors such as variant of pineapples, place of origins, growing seasons, method of collections, storage temperatures and maturity of the pineapples (Najeeb et al., 2020).

Table 1: Overview of pineapple peel characterization of other sources

Cellulose (%)	Hemicellulose (%)	Total Structural Carbohydrates (%)	Lignin (%)	Ash (%)	Crude Protein (%)	Total Extractives (%)	Reference
42.9	20.7	63.6	9.4	2.7	4.6	18.8	This study
40.55	28.69	69.24	10.01	1.5	0.75	-	(Pardo et al., 2014)
20.9	31.8	52.7	10.4	5.9	3.9	28.1	(Banerjee et al., 2019)
32.44	23.2	55.64	19.4	5.27	-	14.5	(Dahunsi, 2019)
35	19.7	54.7	16	4.7	0.33	-	(Khedkar et al., 2017)

Nitric acid hydrolysis optimization by OFAT

From the three OFAT stages of the three important parameters for the recovery of xylose and other byproducts from PP which are fructose, glucose, sucrose, arabinose, and acetic acid. It was determined that the maximum xylose sugar concentration could be produced by using 5 % acid concentration at 105 °C for 20 min residence time that produced to 20 g/L xylose which resulted in to 85% recovery of the xylose from the actual potential xylose sugar in the hemicellulosic. The graphs presented in Figures 3(a), 3(b) and 3(c) illustrate the effects of the acid concentration, temperature, and residence time as independent variables respectively toward the xylose and other byproducts. Since furfural and HMF were detected in such low concentrations, their presence in the graph was not shown. The results indicate that HMF is undetectable for all parameters, whereas furfural is below 1 g/L and 0.05 g/L at the best parameters (5 % acid concentration, 105 °C temperature and 20 min residence time). Inhibitors is one of the issue that cannot be neglected during fermentation as the presence of this inhibitors inhibit the growth of microorganism (Rao et al., 2016). The lower concentration of furan derivatives furfural and HMF in this hydrolysate is a very favorable condition in the fermentation process, as it required no additional pre-treatment for detoxification.

4.2 Effect of acid concentration

For the first stage of OFAT hydrolysis which focuses on varying concentration of acid at 130 °C for 20 min. The result can be seen in Figure 3(a), the highest sugar concentrations of xylose obtained were 15.88 ± 0.37 g/L at 5 % acid concentration. As the concentration increased up to 7 %, the concentration of xylose seems to be decreasing with the other byproducts except for the acetic acids where its concentration increases with the increase of the nitric acid concentration. From the observation it can be seen even at the lowest mild acid concentration, it was proven to degrade the hemicellulose from the biomass by 40 % and increasing up to 67 % at 5% nitric acid. However, a further increase to the 7 % acid concentration resulted in the sugar decomposition reaction occurring with a shorter time, this contributed to the final result of reduced sugar yield.

4.3 Effect of temperature

For the next stage of OFAT hydrolysis which focuses to find the optimum temperature of 5 % nitric acid concentration for 20 min. As seen in Figure 3(b) the concentration of xylose increasing with the temperature increase. However, it dropped as it reach more than 105 °C. The hydrolysis temperature used is quite low which is below 140 °C and a shorter time which is 20 min only. Through the observation of results, these results are quite similar to the study made by Lenihan et al. (2010) namely hydrolysis using dilute phosphoric acid on potato peel. The study also showed clearly that the rate of the decomposition reaction increased with increasing temperature. The reaction takes a shorter time when the temperature is raised however this leads to a rapid rate of sugar degradation. The sugar decomposition reaction begins to overwhelm the production of sugar at high temperatures. It can clearly be seen that an increase in temperature will have a detrimental effect on the rate of sugar production. Hence, explain the pattern of sugar byproducts are the same as xylose.

4..4 Effect of residence time

For the last stage of OFAT hydrolysis which is on residence time variation at 5 % acid concentration at 105 °C. The result in Figure 3(c) demonstrated that the optimum concentration of xylose and glucose was obtained at 20 min residence time which is 16.791 ± 0.08 g/L and 3.33 ± 0.03 g/L. However, as time increasing after 20 min, this sugar concentration decreasing. It is revealed that the hemicellulosic fraction depolymerizes faster at lower temperature than the cellulose fraction with dilute acid treatment while at higher temperature or longer retention time, the formed monosaccharides further hydrolyze to other compounds (Karimi et al., 2006). Thus, 20 min is the best residence time for xylose recovery in the future application.

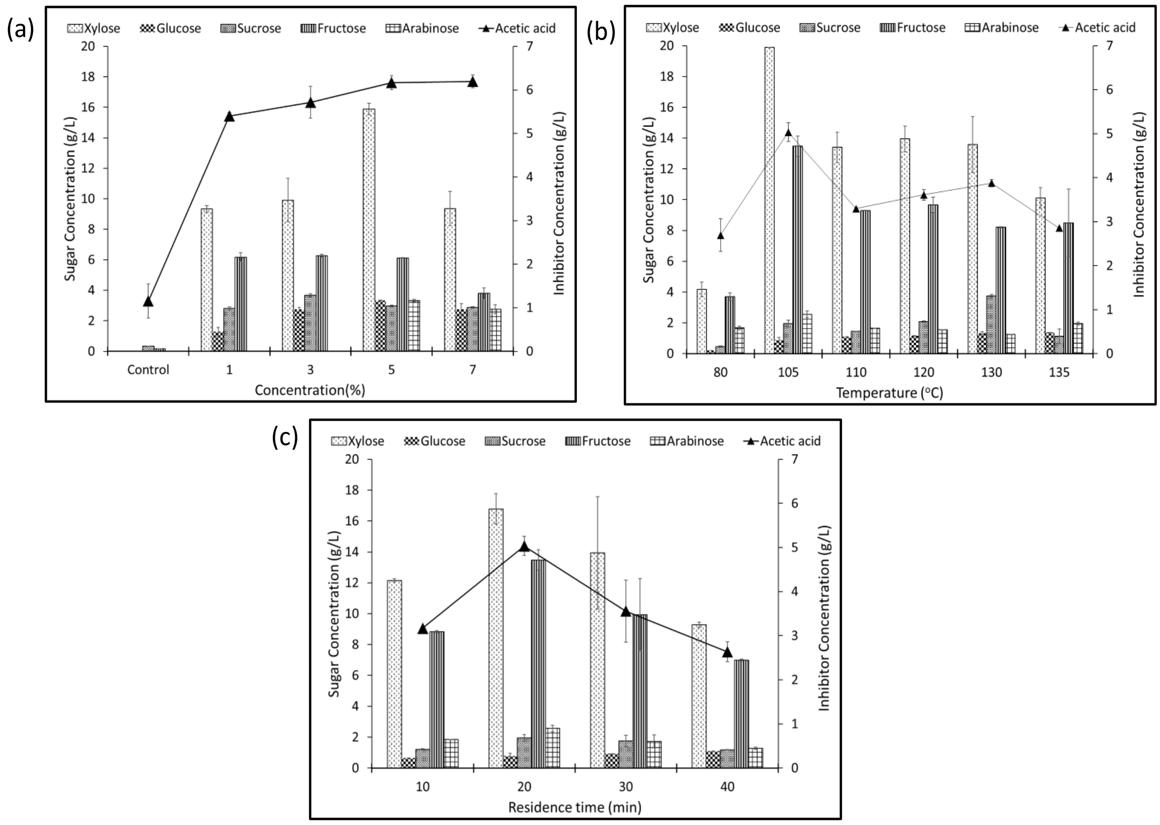

Figure 3: Illustration of the effect of (a) concentration, (b) temperature, and (c) residence time toward the concentration of various sugar and inhibitor, acetic acid

5. Conclusions

The pineapple peel biomass demonstrated excellent potential as a raw material substitute for xylitol production with a maximum xylose concentration of 19.88 g/L at 5 % nitric acid concentration, 105 °C in 20 min. Mild hydrolysis pre-treatment has proven to be a good xylose extraction with 85 % xylose recovery and with lower inhibitor concentration. However, for biotechnology xylitol production, further investigation is required to determine the fermentability of these sugars toward the microbes used in the fermentation process. Thus, with this finding, pineapple peel hydrolysate could be the sustainable fermentation broth without any further pre-treatment for its lower inhibitor concentration of furfural and HMF for the xylitol production. This study is thought-provoking to overcome the current waste disposal issue in Malaysia while generating a substantial income for the pineapple sector from its residual components.

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