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Physical and Chemical Pretreatment of Lignocellulosics in Pineapple (*Ananas comosus*) Peels Dried for Investment

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Abstract. Pineapple (*Ananas comosus*) Peels, once known as waste from agricultural, can be a problem when we eliminate in agriculture and industry. The current technology can help preliminarily to solve this problem. The sustainable solution to this problem is lignocellulosics pretreatments for converted saccharide as a carbon source for ethanol production. The objective of this study is the investigation of pineapple peels pretreatment to produce fermentable sugar by drying and digesting 5% sulfuric acid (H₂SO₄) . And study of cost economic passed selection for investment. The result found that the best investment of drying was 100 °C at 11 hours for the sulphuric acid which could be easily crushed into a fine powder. Moreover, digestion of pineapple peels gave the best total sugar 252.2 g/l by 5% H₂SO₄ incubated for 60 minutes at room temperature. The pineapple peels were digested by 5%H₂SO₄ concentration by incubating for 60 minutes at room temperature, finding to be the best condition and the lowest investment. Finally, the optimisation of investment and management for lignocellulosic pretreatment will improve efficiency of strategy for economic and energy development.

INTRODUCTION

Lignocellulosic biomass is a biological raw material used for countries development such as logistic processing, industrial production, gas production and ethanol production [1]. Thailand is the main countries of agro-industry, have a lot waste agriculture and can apply to energy and environment. Pineapple (*Ananas comosus*) peel (PAP) are wasted from pineapple production process in agro-industry. The main benefit of PAP is low cost value [2] However, the utilization of PAP can produce to agriculture production such as animal feeds, fertilizer, bio-methane and bio-ethanol. Currently, the developing industrial scale operation uses substrate for the converting to ethanol production, Moreover, the PAP is a good carbon source for application a renewable energy [3,4]

Nowadays, alternative energy investment is of general attractive to development country. The investment limited optimization of economic management but The alternative energy in thailand consists of a lot agriculture material as PAP. In this study the best of PAP pretreatment process by using 5% H₂SO₄ and The evaluation of investment were selected. PAP acid dilution pretreatment was utilized for bioethanol production, bio-concrete and pharmaceutical product etc. [5,6]

METHODS

Preparation and Drying processes of PAP

The fresh PAP from Rayong Gold species were used. PAP were washed with distilled water and then cut in 2 cm size with a knife. After that PAP were kept in a vacuum sealed plastic bag at 4°C. The PAP samples were weighed for 10 g in aluminum cups. After that, each samples were dried in a hot air oven with 100°C. Variation of time to dry PAP, the values were calculated such as % dry weight content of PAP, % dry weight (1st formula) and %wet weight (2nd formula) with these formular.[6,7,12]

$$M_w = \frac{(w - d)}{w} \times 100 \quad (1)$$

M_w is wet weight moisture (%)
 w is mass of initial weight(g)
 d is mass dry weight(g)

$$M_d = \frac{(w - d)}{d} \times 100 \quad (2)$$

M_d is dry weight moisture (%)
 w is mass of initial weight(g)
 d is mass dry weight(g)

Composition analysis of PAP

The PAP determination of cellulose, hemicellulose and lignin by NDF determination (Neutral detergent fiber) was added 1 g PAP powder to erlenmeyer flask. PAP sampling was added, neutral detergent solution 100 ml and sodium sulfite 0.5 g. After that, heated to boiling temperature for 60 mins. Filtered and washed 3 times with boiling water. Eventually, was dried for 8 hours at 105°C and let to cool in a desiccator to calculate the 3rd formula and 4th formula [8,9,10]

$$\text{NDF \%} = \frac{(A + B) - A}{C} \times 100 \quad (3)$$

A= weight of crucible
B= weight of residue
C= weight of sample

Neutral detergent solubles:

$$\text{NDS \%} = 100 - \text{\%NDF} \quad (4)$$

ADF determination (Acid detergent fiber) used weight the NDF and add acid detergent solution 100 ml, after that, heat to boiling point for 60 mins. Then, filtered and washed 3 times with boiling water to adjust pH of 7. Finally, dried 8 hours at 105°C and left to cool in a desiccator and calculated with 5th formula [9,10,11]

$$\text{ADF \%} = \frac{(A + B) - A}{C} \times 100 \quad (5)$$

A= weight of crucible
B= weight of residue
C= weight of sample

Acid detergent lignin (ADL) determination was used to weight from ADF determination and add 25 ml of 72 % H₂SO₄, After that, carried on cool extraction during 3 hours and stirring every hours, filtered and washed 3 times

with boiling water to adjust pH of 7. Then dried to 8 hours at 105 °C left to cool in a desiccator. Ash in a muffle at 550 °C to 2 hours , left cool in a desiccator. Calculate with 6th, 7th and 8th formula [9,12,13]

$$ADL \% = \frac{(A + B) - A}{C} \times 100 \quad (6)$$

A= weight of crucible

B= weight of residue

C= weight of sample

$$\% \text{ Hemicellulose} = \% \text{ NDF} - \% \text{ ADF} \quad (7)$$

$$\% \text{ Cellulose} = \frac{(\% \text{ ADF} - W_1)}{\text{weight of PAP}} \times 100 \quad (8)$$

Dilute sulfuric acid pretreatment

The dilute sulfuric acid was prepared 5 ml in a volumetric flask 100 ml (5%v/v) with ratios of PAP and H₂SO₄ 5%v/v were 1:20, 1:50 and 1:100 for 0, 15, 30 and 60 min, respectively. After that, they were centrifuged (HERMLE Mettler Toledo, Switzerland) with 5,000 rpm/min at 10 min . Solid residue was collected by filtration and washed with 300 ml of distilled water to remove residual sulfuric acid, then air dried at 105 °C for 12 h [8,9]. PAP supernatant was calibrated with 1 N of sodium hydroxide(NaOH). Then pH, total soluble solid, total sugar and reducing sugar were measured.[10,11,12].

Economic calculations

The best condition of PAP was to select economic calculations such as Net present value (NPV), Return On Investment(ROI) and Payback Period. They were used from the 9th, 10th and 11th equations.[13,14,15,16]

$$NPV = \sum_{t=0}^N \frac{CF_t}{(1+r)^t} \quad (9)$$

CF = Cash flow

r = Required rate of return

t = year of cash flow

N = the nth year

$$\text{Return On Investment} = \frac{((\text{Discounted Benefits} - \text{Discounted Costs}))}{(\text{Discounted Costs})} \quad (10)$$

$$\text{Payback Period} = \text{Number of years prior to full recovery} + \frac{((\text{Unrecovered cost at start of year}))}{(\text{Cash flow during full recovery year})} \quad (11)$$

RESULTS AND DISCUSSION

PAP drying process

The factor for selection of PAP drying process consisted of time and temperature. The result showed that the percentage dry weight of PAP of drying process with 100°C gave 17.94±1.77% at 11 h. The percentage dry weight moisture and wet weight moisture of PAP were 0.59±0.12 and 82.06±1.79%. The relationship between time and temperature for drying gave the same drying theory, which moisture in PAP can be removed with high temperature. The increasing temperature can decrease time of drying process. The results are consistent with the theory that high temperatures can reduce the amount of drying time and falling drying rate [14,15] This result showed that drying technique at 100 °C for 11 hours with a hot air oven can be used to establish an optimized drying schedule for the

shortest drying time and good PAP dried quality. On the other hand, the colour characteristic of PAP was changed from a yellow color to a black color (figure 1) because PAP drying had an oxidation reaction in PAP [16,17,18]

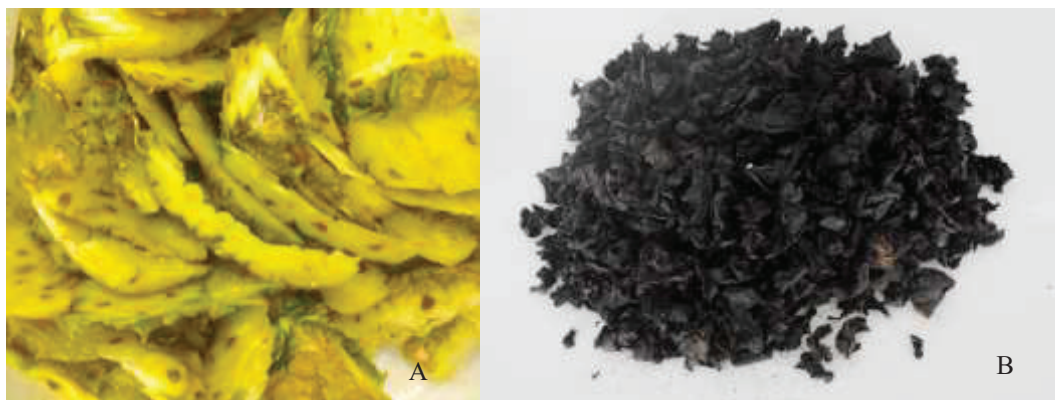


FIGURE. 1. The colour of PAP were A : before drying (yellow color) and B : After drying at 100 °C 11 h (black color)

The composition of PAP

The determine of PAP drying for 100 °C at 11 h with Van Soest and Wine method gave the composition of cellulose 23.03 ± 2.14 %, hemicellulose 59.26 ± 0.63 % and lignin 4.19 ± 0.56 % (Figure 2). Choonut et al.[19] studied of composition of untreated pineapple peel that gave cellulose 21.98 ± 2.34 %, hemicellulose 74.96 ± 2.55 % and 2.68 ± 1.54 %. While, Pardo et al. [20] studied of chemical characterisation of the industrial residues of PAP that gave cellulose 43.53 ± 1.17 %, hemicellulose 21.88 ± 0.22 % and lignin 13.88 ± 1.70 %. The result of PAP determination (cellulose, hemicellulose and lignin) were difference from the study of Choonut et al. [15] and Pardo et al.[16]. As a result there were differences that occurred due to plant species, a rearing, land, fertilization and temperature.

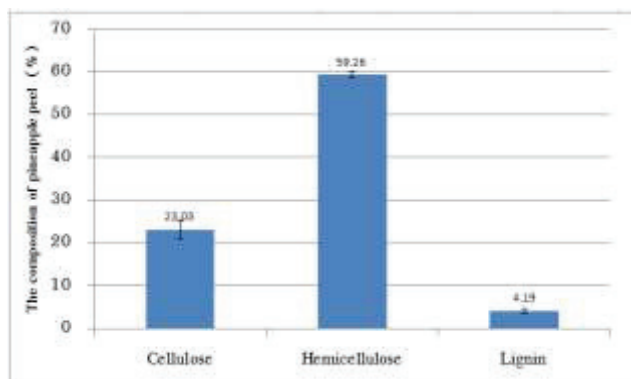


FIGURE. 2 : The composition of PAP with Van Soest and Wine method

Effect of PAP was pretreated with $5\%H_2SO_4$ at room temperature of the ratio 1/20, 1/50 and 1/100. All conditions were kept at 0, 15, 30 and 60 minute to determine total soluble solid, pH, solid residue, total sugar and reducing sugar. The result shows that PAP residue after pretreatment time at 0, 15, 30 and 60 mins were decreased in weight to 0.3251, 0.2985, 0.2585 and 0.2152 g (in condition of ratio 1/20), respectively. PAP residue weight of ratio 1/50 decreased to 0.1525, 0.1125, 0.0985 and 0.0875 g, respectively. PAP residue of ratio 1/100 were decreased 0.0685, 0.0558, 0.0456 and 0.0378 g, respectively. PAP residue after pretreatment with $5\%H_2SO_4$ were at the highest decrease at 60 mins pretreatment at room temperature.

The result of supernatant of PAP pretreatment assayed pH, shows that the comparison of all conditions before pretreatment, equalled to pH 2.0 and after pretreatment equalled to pH 1.81. (Figure. 3). PAP pretreatment before and after controlled time at 0, 15, 30 and 60 min. Total soluble solid of dilution 1/20, 1/50 and 1/100 before pretreatment (1, 0.5 and 0.67 % brix) and after pretreatment (1, 0.67 and 1.17% brix) at 0 min., before pretreatment

(1, 0.5 and 0.67 % brix) and after pretreatment (1, 1 and 1.17% brix) at 15 min., before pretreatment (0.67, 1.0 and 0.5 % brix) and after pretreatment (1.17, 1 and 1 % brix) at 30 min. and before pretreatment (0.67, 0.83 and 0.5 % brix) and after pretreatment (1.67, 1.33 and 1.50 % brix) at 60 min, respectively. (figure 4). The results show that total soluble solid increases with longer release of the PAP pretreatment.

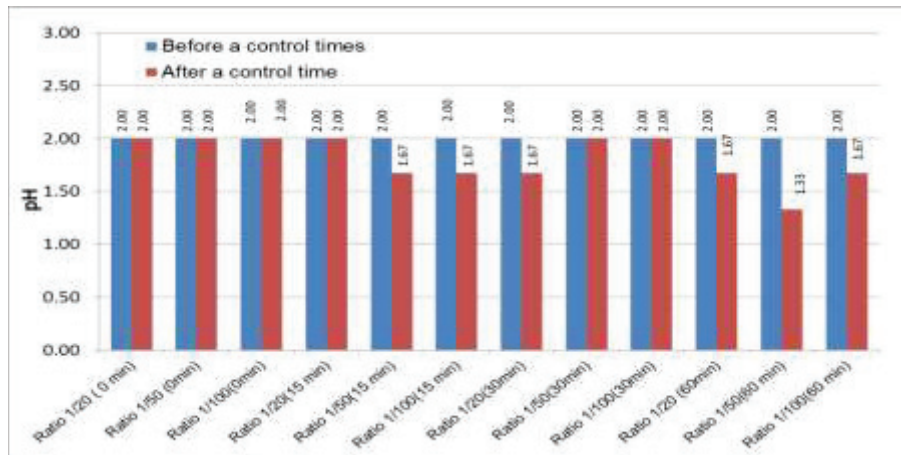


FIGURE 3. The pH of PAP pretreated with 5 % H₂SO₄ (ratio 1/20, 1/50 and 1/100 g) at 0, 15, 30 and 60 mins.

The highest content of the total sugar was 252.28 g/L in condition of PAP 1 g per 100 ml of 5% H₂SO₄ for 30 mins and the highest content of reducing sugar was 158.92 g/L in condition of PAP 1 g per 100 ml of 5% H₂SO₄ for 60 mins. In showed of the table. 1.

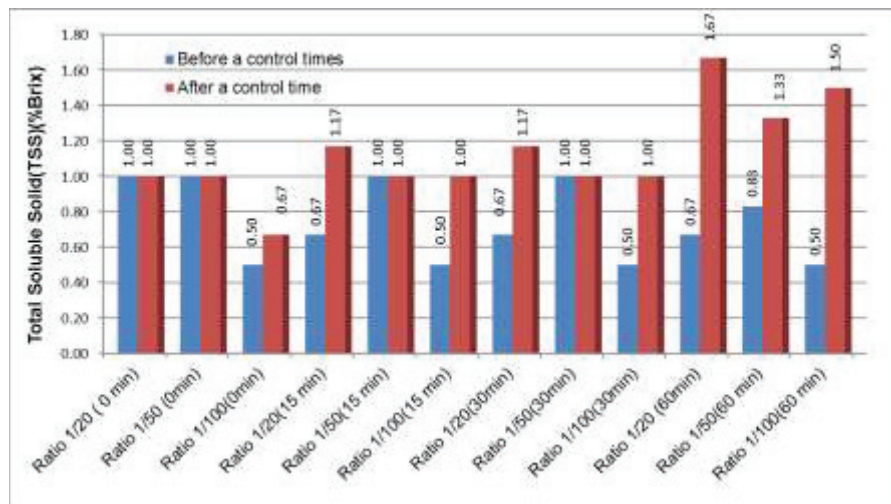


FIGURE 4. Total soluble solid (% brix) in before and after pretreated with 5% H₂SO₄ in all condition of PAP

The calculation of economic value for investment of best condition of PAP pretreatment was PAP 1 g of dry weight per 100 ml of 5 % H₂SO₄ at room temperature for 30 mins. The separation of condition was solid residue and solution (table 1.). The solid residue had 231.682 kg per year, to convert revenue to 23168.2 bath (Assume 1 kg of solid residue was a hundred bath). This solid residue could be applied to Wall, Concrete Building and household furnishings etc. The solution of PAP pretreatment was 259.18 L per year. This solution was a high substrate value for purification to monosugar which was converted to renewable energy in industrial as biogas, methanol, ethanol and butanol production etc.[21,22] It provides revenue about three hundred thousand bath. When The NPV calculation of economic value using first equations were 105,736.28 (table 3; table 4). This production had Return On Investment (%ROI) at 5.21 % and Payback Period was about 3 years.

TABLE 1 Solution of PAP pretreatment with 5% H₂SO₄

Ratio (PAP (g)/ 5 %H ₂ SO ₄ (ml))	Time (min)	Total sugar (g/L)	Reducing sugar(g/L)
1/20	0	150.32±0.01	76.98±0.01
1/50		177.43±0.01	76.45±0.01
1/100		171.43±0.01	76.27±0.00
1/20	15	171.26±0.02	97.70±0.01
1/50		211.51±0.02	92.07±0.01
1/100		210.68±0.01	94.48±0.02
1/20	30	203.40±0.05	105.09±0.03
1/50		220.39±0.04	120.57±0.01
1/100		236.28±0.00	127.45±0.00
1/20	60	210.63±0.04	126.67±0.00
1/50		225.58±0.03	133.46±0.01
1/100		252.28±0.03	158.92±0.61

TABLE 2 Cost analysis of the selective of PAP pretreatment for investment.

Cost of raw materials	UnitX365 days (1 Year)	Total balance (Bath)
H ₂ SO ₄	500X365	182,500
PAP (fresh)	13,035.714 Kg of fresh weight /year = 356 Kg of drying/ year	0
Logistic	1 unit (5,000 bath)/year	5,000
Hot air oven (100 °C at 7 h.)	1 Unit = 58.96 Bath 1 Unit = 1.5 KW X 7 h = 10.50 Unit Calculate per day = 10.50 Unit X 58.96 Bath = 619.08 Bath/day	225,964.3
Strainer	1	15,000
Other	1	10,000
	Total	438,464.30

TABLE 3. The NPV calculation for investment in PAP pretreatment.

	Years					Total
	1	2	3	4	5	
Benefits(฿)	323,168.20	646,336.40	1,292,672.8	1,292,672.8	1,292,672.8	4,847,523.0
Costs(฿)	438,464.30	438,464.30	438,464.30	438,464.30	438,464.30	2,192,321.5
Cash Flow(฿)	- 115,296.10	207,872.10	854,208.50	854,208.50	854,208.50	2,655,201.50

TABLE 4. The NPV result of years investment

Year	NPV
1	-104814.64
2	-121795.12
3	1641.78
4	1583.44
5	1530.40
	105,758.23

CONCLUSION

The increase temperature for drying could decreased times. The case study found that at 100 °C for 11 hours drying gave 17.94±0.18% dry weight content of PAP, 0.59 ± 0.17% dry weight and 82.06±1.78% wet weight. The major component of PAP gave cellulose content (23.03±2.14%), hemicellulose content (59.26±0.63%) and lignin content (4.19±0.57%). The structure of PAP was not destroyed. The best condition of this study was found to be a ratio of 1 g of dry PAP /100 ml of 5% H₂SO₄ at 30 mins as room temperature for pretreatment processes. The investment gave a Net Present Value (NPV) (105,758.23), Return On Investment (%ROI) (5.21%) Payback Period (3 year).

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