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Hydrothermal pretreatment and acid hydrolysis of coconut pulp residue for fermentable sugar production

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ABSTRACT

Coconut pulp residue is the waste generated after the extraction of milk and oil. This material became an interest as feedstock for the production of biofuels and other bioproducts in a biorefinery context. The present study aimed to improve the release of sugar from coconut pulp residue through the optimization of sequential hydrothermal and acid pretreatment. An experimental design was constructed with the central composite design (CCD) response surface method using factors of the hydrothermal residence time of 20, 40, 60 min and post-acid treatment concentration of 1%, 2% and 3% (v/v) in constant temperature and time of 121 °C and 20 min. Total sugar yields of 32.47, 27.51 and 26.72 g/L were observed after hydrothermal pretreatment time of 20, 40 and 60 min, respectively. Furthermore, when the pretreated solid residues were subjected to acid pretreatment, the results revealed an increment of 90% on reducing sugars after reaction with 1%, 2% and 3% H_2SO_4. Statistically, the optimum condition for the two-stage hydrolysis of coconut pulp residue was 60 min hydrothermal pretreatment followed by 3% H_2SO_4 acid hydrolysis with maximal reducing sugar release of 120.71 g/L. In addition, the degree of polymerization achieved was 1.2, indicating no further hydrolysis required. The current study demonstrates that two-stage pretreatment improves saccharification and provide sufficient sugars for the fermentation process.

1. Introduction

Fuel is an essential factor in daily human life. Carbon dioxide emissions, global warming, acid rain, and urban smog are one of those damages generated using fossil fuels. Moreover, several countries are seeking new forms of alternative energy sources, which guarantees long-term energy security and reducing carbon dioxide from the use of fossil fuels. Hence, this phenomenon had shifted toward the production of biofuels from renewable resources (Vu et al., 2018). These materials aim to produce biofuels in an environment-friendly approach that will limit the effect on climate change and global oceanic acidification and, more importantly, decrease the dependence on fossil fuel (Dien et al., 2009). The use of biofuels is an emerging alternative solution to reduce the consumption of fossil fuels and its by-products that negatively affects the environment (Gonçalves et al., 2014).

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Bioethanol is one of the most attractive fuel being renewable and sustainable, having higher oxygen content and octane number, among others (Putra et al., 2015). Normally, ethanol is being produced from the conversion of glucose from the feedstock to ethanol through fermentation. Biomasses containing a significant amount of sugars produces high ethanol yield (Wang et al., 2008). At present, massive production of bioethanol is mainly dependent on sugar crops such as sugarcane and sugar beet, which accounts for about 40% of the total bioethanol produced and almost 60% from starch crops. However, this creates a significant concern of competition between food and fuel. Hence, it is necessary to look for alternatives from non-food energy sources to minimize the conflict between land use for food production and energy feedstock production.

Lignocellulosic biomass is a primary candidate for alternative energy because of its great abundance, low-cost and widespread availability (Ruan et al., 2019). It serves as a renewable feedstock for production of biofuels and value-added biochemical that contributes immensely to sustainable growth of the economy (Zhang et al., 2019). These biomasses are mainly generated from food and energy sectors, which include agricultural residues, energy crops, forestry residues, and yard trimmings (Ge et al., 2016; Lin et al., 2019). However, bioethanol production from lignocellulosic biomass remains to be a challenge due to their complex cross-linked structure in which the sugar-rich cellulose and hemicellulose are covered with a recalcitrant protective layer of lignin (Conesa et al., 2016). The lignin prevents the chemical or enzymatic hydrolysis of cellulose and hemicellulose to fermentable sugars (Ramaraj and Unpaprom, 2019). The pretreatment is a necessary step to alter the structure of lignocellulosic biomass to increase the digestibility of cellulose and hemicellulose. Moreover, make it accessible for efficient saccharification (Sindhu et al., 2015).

Pretreatment strategies that are extensively used in numerous biomasses include chemical pretreatment (acids, alkali), biological pretreatment (fungi), physical pretreatment (grinding, chipping, and milling) and combination of all of them (Sharma et al., 2019). By far, hydrothermal pretreatment is one of the most effective pretreatment to different types of biomass for bioethanol production (Zakaria et al., 2015). This method is environment-friendly as it only contains the lignocellulosic biomass and water in the reaction. In the process, hydronium ion present from the water acts as an acid catalyst causing the release of acetate from xylan and hydrolysis of glycosidic bonds in the xylan of the biomass (Kapu et al., 2016; Pedersen et al., 2010; Ruiz et al., 2020). These particular reactions cause hydrolysis of hemicellulose polysaccharides to monomers and oligomers. However, oligomers cannot be directly fermented to ethanol by most organisms and therefore succeeding enzymatic or chemical hydrolysis are needed to convert oligomers into sugar monomers (reducing sugar) that are amendable to downstream fermentation (Zhang et al., 2015).

In particular, a broad hemicellulolytic enzyme are required to hydrolyze the oligomers into fermentable sugars – causes additional cost mainly due to longer residence times and considered unfeasible to large-scale application. On the other hand, hydrothermal pretreatment also affects the cellulose and lignin, but to a limited extent. Crystallinity and degree of polymerization of cellulose are slightly affected by hydrothermal pretreatment. Amadi et al. (2018) presented the effect of hydrothermal pretreatment at 100 °C (boiling) of 30 min to pseudo-stem waste. It was found out that the cellulose increased significantly with a moderate increment in reducing sugars. Similarly, Chen et al. (2016) hydrothermally treated the sugarcane bagasse at 140–220 °C for 20 min to enhance the enzymatic digestibility of the substrate (Zhuang et al., 2015).

The enzymatic digestibility of the sugarcane bagasse was improved with increasing pretreatment severity, which is attributed to the partial removal of amorphous components, mainly hemicellulose. Consequently, hydrothermal pretreatment is less effective on lignin, especially in severe or harsh conditions. Lignin has shown the formation of droplets that redeposit or combine with cellulose surface when subjected to hydrothermal pretreatment which in turn hinder enzymatic digestibility (Donohoe et al., 2008). In a series of test of Li et al. (2014) in poplar wood, lignin migrated and coalesces within and out of the cell wall and deposited on the cellulose and inhibits the further hydrolysis. Alternatively, the hydrothermal pretreatment are commonly followed by acid hydrolysis which are widely used to treat lignocellulosic biomass rich with cellulose and hemicellulose (Keskin et al., 2019). Acid hydrolysis is favored over other pretreatment because of its efficient saccharification of hemicellulose and oligomers to monomers while causing structural changes to the solid fractions for better accessibility and conversion (Loow et al., 2016; Toquero and Bolado, 2014; Zheng et al., 2018). Acid breaks the matrix structure of the fiber into cellulose, hemicellulose, and lignin components first followed by conversion of these polysaccharides into monosaccharides (Bajpai, 2018). The major advantage of acid hydrolysis over other techniques is that it results in a higher sugar yield and good reproducibility (Chen, 2015).

However, formations of inhibitory compounds are in consideration. In contrast, several studies have demonstrated the applicability of dilute acid to avoid the formation of such compounds. Rojas-Chamorro et al. (2020) examined the effect of 1–3% sulphuric acid concentration on brewer spent grain. It was found out that hydrolysates generated low concentrations of inhibitors that would not affect the downstream processes. On the other hand, several literatures have demonstrated the effectivity of subsequent application of hydrothermal and acid hydrolysis, especially to high-hemicellulose containing biomass. Zhang et al. (2015) kinetics in xylo-oligosaccharides from hydrothermal and acid hydrolysis of corn stover revealed a 100% fermentable sugar recovery from low-temperature and acid condition. The efficiency of the method was also exhibited in a study of Kim et al. (2013a,b), whereas the increase in fermentable sugar yield from wood-derived xylo-oligosacharride were presented using high acid loading in low temperature. As a summary, the advantages and disadvantages of hydrothermal pretreatment and acid hydrolysis are presented in Table 1.

Coconut is widely cultivated in Asia, Oceania, Latin America and Africa and concluded a total of 60 million tons production in 2017 (FAOSTAT, 2019). It has several applications mainly in food, beverages and as a source of wood and handcrafts. Given its wide functionalities, one of the most prominent products from coconut is the virgin coconut oil. World coconut oil production has been growing over the past years, primarily because of greater global demand. In particular, the global coconut oil production inclined to 3.65 million metric tons in 2019 from 3.34 in 2015. The industrialization of coconut oil production, however, generates a huge amount of pulp residue, whereas in 2019 alone has created 1.9 million metric tons. Coconut pulp residue is a by-product waste

Table 1 – Advantages and disadvantages of hydrothermal pretreatment and acid hydrolysis (Pino et al., 2019; Ruiz et al., 2020; Solarte-Toro et al., 2019; Ximenes et al., 2017; Zanuso et al., 2017).

	Advantages	Disadvantages
Hydrothermal pretreatment	No addition of catalysts or chemicals	Water demanding
	Hemicelluloses are converted into soluble compounds	High energy requirement
	Little corrosion on equipment	Lignin are partially solubilized
	Enhances enzymatic digestibility	
	Low formation of inhibitory compounds	
	Reduced capital and operational cost	
Acid hydrolysis	Extensively used in large scale	Formation of inhibitory compounds
	Hemicellulose are hydrolyzed to monomeric sugars	High investment on reactor construction
	Solubilizes part of the lignin and cellulose, releasing oligomers and carbohydrates	Equipment corrosion and acid recovery problems

from the extraction of coconut milk and oil from coconut meat. Usually, coconut pulp residues are used as fertilizer, feed to animals, and enormous quantity is being discarded in inappropriate locations (Sulaiman et al., 2013). Such practices cause pollution, waste disposal problem, and an increase in handling costs for farmers.

Hence, it is essential to find marginal solutions for the proper appropriation of coconut pulp residue into an economically valuable product. Recent studies have demonstrated the feasibility of coconut waste, including shell and husk for bioethanol production (Hossain et al., 2017; Sulaiman et al., 2013). However, limited studies are available on coconut pulp residue as feedstock for bioethanol production. According to Sangkharak et al. (2019), coconut pulp residue contains a vast amount of hemicellulose and cellulose that are potentially hydrolyzable into fermentable sugars. However, at present, the pulp residue has not yet been well explored in sequential pretreatment and hydrolysis for improved sugar released. The utilization of sequential hydrothermal and acid hydrolysis for coconut pulp residue would be highly desirable since it will improve the release of fermentable sugars necessary for bioethanol production.

Moreover, the use of coconut pulp residue in the production of advanced biofuels such as ethanol would be highly desirable since it will add up value to products of coconut oil and milk manufacturing and assure sustainable alternative to fossil fuels. In this study, coconut pulp residue was pretreated with hydrothermal pretreatment and acid hydrolysis to produce a high quantity of sugars. Optimization of pre-hydrothermal treatment time and acid concentrations using response surface methodology were also conducted in order to search for the possibility of interaction between the factors tested to achieve the highest yield of fermentable sugars.

2. Materials and methods

2.1. *Raw material preparation*

Coconut pulp residues were obtained after the removal of oil from a local oil processing company (Ampol Food Corporation Company Limited) in Chiang Mai, Thailand. Two (2) mm particle size of pulp residue biomass was dried in an economy laboratory oven (Binder ED-115, Germany) at 60 °C for 48 h until constant moisture content was achieved. All analytical chemicals were obtained from Sigma Aldrich USA or Merck, Germany.

2.2. *Determination of lignocellulosic components*

The percentage of cellulose, hemicellulose and lignin of coconut pulp residue were analyzed using the neutral detergent (NDF), acid detergent fiber (ADF) and acid lignin (ADL) standard method described by Van Soest et al. (1991). One gram (1 g) of coconut pulp residue was mixed with 100 mL of NDF and 0.5 g of sodium sulfite. The mixture was then boiled in a reflux system for two hours. The crucibles and samples were washed with hot water and acetone three times using cold extraction unit (FT 121 Fibertec^{TM}, Denmark). After washing, the crucibles and samples continuously added with ADF solution and heated by hot extraction unit (FT 122 Fibertec^{TM}, Denmark) for 1 h and 30 min. For ADL, the residues recovered in ADF were subsequently treated with 72% H_2SO_4 for 3 h. After the reaction, the crucibles were washed with boiled water, distilled water, acetone and dried for 4 h at 105 °C, kept in a desiccator and weighed until constant. The percentage of lignin, cellulose and hemicellulose are calculated based on the following formulas:

$$\%Lignin = \%ADL \tag{1}$$

$$\%Cellulose = \%ADF - \%ADL \tag{2}$$

$$\%Hemicellulose = \%NDF - \%ADF \tag{3}$$

2.3. *Hydrothermal pretreatment*

Hydrothermal pretreatment, developed by Amadi et al. (2018), was applied to the coconut pulp residue. Low severity of pretreatment (100 °C) was applied to avoid the formation of inhibitors (Kim et al., 2013a,b). The pretreatment of coconut pulp residue consisted of the mixed substrate with 200 mL distilled water at 5% biomass loading (w/v) in a 250 mL Erlenmeyer flask. The flask was set to the electrothermal heating mantle (HTS-1003, Japan) and heated under target temperature of 100 °C for different residence times of 20, 40 and 60 min (excluding 20 min heat-up time). After pretreatment, each flask was cooled to room temperature and filtered through 1 layer of cheesecloth. The resulting solid fractions were carried over into the post-acid treatment/hydrolysis and the liquid portions were subjected to sugar concentration estimation using phenol sulfuric acid method and dinitrosalyclic acid (DNS) methods.

2.4. Post-acid pretreatment/hydrolysis

Post-acid pretreatment/hydrolysis of the pretreated solids was done based on the method described by Sritrakul et al. (2017). The concentration of sulphuric acid (H_2SO_4) was varied to 1%, 2% and 3% (v/v). This post-treatment was accomplished by 15% (w/v) pretreated solid residues with 15% moisture content, which was added to 60 mL of diluted H_2SO_4 solutions in a 250 mL capped Erlenmeyer flask. The flask was heated to 121 °C at 15 psi for 20 min (excluding 10 min heat-up time) using a vertical pressure steam sterilizer (LS-35 LD, China). Upon the completion of the reaction, the sterilizer was depressurized and the flask was removed and cooled using ice-water for 5 min. The pretreated solution was then filtered to isolate the liquid hydrolysate. The amounts of total and reducing sugar were determined using phenol sulphuric acid and DNS method which was adopted from our previous publications (Bautista et al., 2019; Casabar et al., 2019; Manmai et al., 2020; Ramaraj and Unpaprom, 2019; Vu et al., 2018).

2.5. Sugar analysis

Miller (1959) and Dubois et al. (1956) methods were used to analyzing the reducing and total sugar concentrations of liquid hydrolysate from sequential pretreatment and hydrolysis. The phenol-sulfuric acid method was carried out with diluted 0.5 mL of sample combined with 0.5 mL of 5% phenol and 2.5 mL of 98% sulphuric acid (Dubois et al., 1956). The solution was kept for 10 min and the absorbance was read using the spectrophotometer (Drawell-DV-8000, China) at 490 nm. Reducing sugar was estimated by diluted 0.5 mL of sample and added with 0.5 mL of 3,5-dinitrosalicylic acid (DNS) solution and heated in a boiling water bath for 15 min followed by addition of 4 mL of distilled water (Miller, 1959). The mixture was then cooled to room temperature and the absorbance was measured at 540 nm using a spectrophotometer. Glucose was used as the standard.

Sugars and acetic acid, propionic and citric acid concentration of liquid phase from the optimum hydrothermal pretreatment and acid hydrolysis condition were analyze by high-performance liquid chromatography (HPLC) (condition: mobile phase–5 mM H2SO4; flow rate-0.7 mL/min; the temperature of the column: 60 °C; Hi-Plex H column).

2.6. Optimization with response surface methodology

The interaction between the pre-hydrothermal treatment time and acid concentration on the release of sugars can easily be determined using response surface methodology. The hydrothermal residence time and the sulfuric acid concentration were chosen as independent variables. The amount of reducing sugars was used as dependent variables for the central composite design response surface optimization.

The central composite design is used in optimization of analytical procedures and limited into 2 factors as higher factors causes inefficiency in the modeling of quadratic functions (Khuri and Mukhopadhyay, 2010). In this design, there are three experimental levels: −1, 0, 1 as presented in Table 2. Total runs for the response surface optimization were 27 and three replicates for each run were employed to verify any changes in the estimation and experimental procedure. Design expert (Version 12.0, Stat-Ease Inc. Minneapolis, USA) was used for the statistical analysis of the model for the reducing sugars from the coconut pulp residue.

Table 2 – Reducing concentration parameters and their values used for the experiment.

Factors	Unit	−1	0	1
Hydrothermal pretreatment time	mins	20	40	60
Acid concentration	% (v/v)	1	2	3

3. Results and discussion

3.1. Lignocellulosic composition of coconut pulp residue

The lignocellulosic composition of coconut pulp residue in this study was 35.45 ± 0.13% of cellulose, 43.90 ± 0.26% hemicellulose and 18.16 ± 0.28% lignin. The compositions obtained were similar to the previously reported study on coconut pulp residue by Sangkharak et al. (2019), who reported 36.1 ± 0.1% cellulose, 44.1 ± 0.1 hemicellulose and 16.3 ± 0.01% of lignin. Evidently, hemicellulose has the most in the lignocellulosic component, followed by cellulose and lignin.

In comparison with cellulose, hemicellulose is amorphous and, therefore, more susceptible to hydrolysis, particularly with the use of hydrothermal pretreatment. High amounts of monomeric sugars, mostly in oligomeric forms, can be extracted in hemicellulose as reported by Garrote et al. (1999) and Mok and Antal (1992). However, hydrothermal pretreatment is usually followed by acid hydrolysis to convert unfermentable oligomer to monomeric sugars, which are essential for ethanol fermentation. Kinetics studies presented by several literatures show sugar yields are immensely improved when two-stage hydrothermal and acid pretreatment are applied (Aguilar et al., 2002; González et al., 1986; Kim et al., 2013a,b; Liu et al., 2012; Yat et al., 2008). Since coconut pulp residue composed mainly of hemicellulose, hydrothermal pretreatment and post-acid hydrolysis might be a suitable method to saccharified the coconut pulp residue.

3.2. Effect of hydrothermal pretreatment

Previous studies have proved the efficiency of hydrothermal pretreatment to biomasses and have shown work effectively at a commercial scale (Kumar et al., 2011; Negro et al., 2003; Nitsos et al., 2013; Petersen et al., 2009; Saha et al., 2013). In this study, coconut pulp residues were treated in 100 °C temperature at different heating times of 20, 40 and 60 min. The process condition of the pretreatment was based on the findings of Kim et al. (2013a,b), where low severity conditions are favorable to avoid the production of unwanted by-products. To explore the influence of the hydrothermal pretreatment, total sugar and reducing sugar release of coconut pulp residue were presented in Fig. 1. For the untreated substrate (control), total sugar was found to be 21.97 g/L and the reducing sugar was 5.43 g/L. After the hydrothermal pretreatment, total sugars significantly increased after 20 min of treatment (32.47 g/L) and gradually decreased with increasing heating times.

The increment of total sugars is due to the release of hydronium ion from hydrothermal pretreatment that causes depolymerization of hemicellulose, which in turn forms acetic acids and uronic acids (Nitsos et al., 2013). The release of such acids is thought to hydrolyzed hemicellulose and oligosaccharides (Pu et al., 2013; Sun et al., 2015). On the other hand,

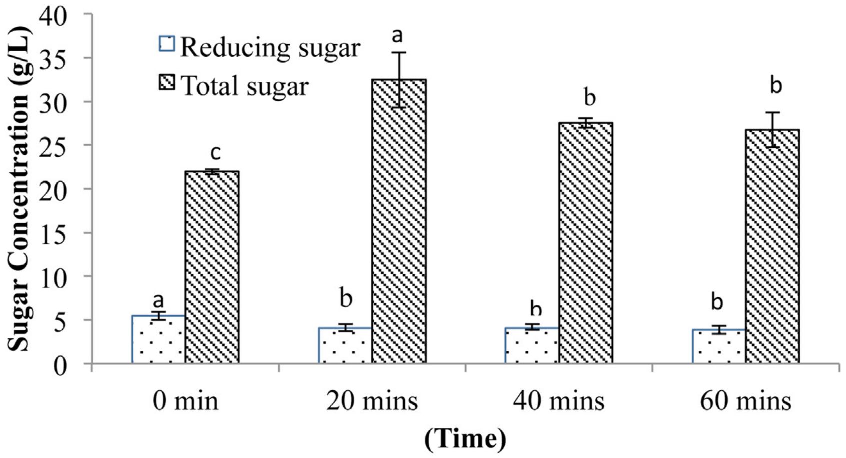

Fig. 1 – Sugar concentrations of coconut pulp residue from hydrothermal pretreatment step. Data are presented as means ± SD of three replicates. Columns with the same letter are not significantly different ($p < 0.05$) from each other using one-way ANOVA followed by Tukey's multiple comparison tests.

the moderate reduction of total sugars after 40 and 60 min hydrothermal pretreatment can be attributed to the degradation of cellulose due to longer exposure to heat (Zou et al., 2019). The significant decrease in total sugar after pretreatment with 60 min was in line with the reports of Amadi et al. (2018) showing the adverse effect of excessive application of heat.

Consequently, the reducing sugars of coconut pulp residue showed a minimal decrease with the application of hydrothermal pretreatment. According to Chen et al. (2018), hydrothermal pretreatment at 100 °C produces C_4–C_6 oligomers from the few short glucose chains present in the amorphous section of cellulose bonded to crystalline cellulose through hydrogen bonding. In this work, hydrothermal pretreatment was carried out at 100 °C, which therefore resulted in decrementing of reducing sugar and formation of oligomers (represented in the total sugar). The formations of oligomers are typical for hydrothermal pretreatment, as the conditions leading to the highest recovery of soluble hemicelluloses do not lead to its complete hydrolysis (Carvalheiro et al., 2009). Nevertheless, the findings of the study were similar to the report of Ding et al. (2017) and Li et al. (2016).

3.3. *Optimization of post-acid hydrolysis*

Acid hydrolysis has been regarded as a rapid and convenient method in converting cellulose, hemicellulose and oligomers into fermentable sugars amendable for downstream processing (Kong-Win Chang et al., 2018; Nakasu et al., 2016; Rojas-Chamorro et al., 2020). In this stage, hydrothermally pretreated coconut pulp residue was digested further using acid hydrolysis. The solid fractions recovered from hydrothermal pretreatment of coconut pulp residue at 100 °C for 20, 40 and 60 min was treated with 1%, 2% and 3% (v/v) sulfuric acid concentrations at the temperature of 121 °C in a vertical pressure steam sterilizer for 20 min. Table 3 shows the resulting reducing sugars at each pre-hydrothermal pretreatment time and acid concentration. Based on the results, as pre-hydrothermal treatment time increases, reducing sugar increases rapidly, providing almost 90% increase in yield when time is increased from 20 to 60 min for the same acid concentrations.

Table 3 – Experimental design and results for dilute acid pretreatment of coconut pulp residue used for the Central Composite Design response surface optimization.

Run	Hydrothermal Pretreatment (min)	H_2SO_4 Conc. (%)	Reducing sugar (g/L)
1	40	2	107.86
2	60	2	112.86
3	60	1	93.93
4	20	2	95.71
5	40	1	90.14
6	40	2	110
7	20	1	11.71
8	40	2	103.57
9	60	3	120.71
10	60	2	107.86
11	60	3	117.14
12	40	3	110
13	20	3	10.79
14	20	2	94.28
15	20	1	11.71
16	40	3	107.14
17	20	3	10.07
18	20	2	95.71
19	60	1	88.57
20	20	1	11.43
21	40	3	111.43
22	60	2	115
23	60	1	99.29
24	40	1	90.71
25	40	3	110
26	20	3	10.07
27	60	3	124.29

In addition, increasing acid concentration has also shown a significant effect on reducing sugars. As the acid loading increases, the concentration of reducing also increases. The values range from 9.59 to 11.62 g/L in 20 min, 89.52 to 109.52 g/L in 40 min and 93.93 to 120.71 g/L in 60 min. The increase in reducing sugar with increasing acid concentration is due to the acid capability to act as catalysts that result in protonation of the oxygen atom of the glycosidic linkages. The cleavage of glycosidic linkages leads to the degradation of polymers into reducing sugars or simple sugars such as glucose, xylose, and arabinose, as well as lignin fragments Harmsen et al. (2010) and Loow et al. (2016).

To stimulate the effect of pre-hydrothermal treatment time and increasing acid concentration (1–3%, v/v), experimental data were fitted and statistically optimized using response sur-

Table 4 – Parameter estimates and analysis of variance (ANOVA) of the design for production of reducing sugars from hydrothermal and post-acid pretreatment.

Source	Sum of squares	df	Mean square	F-value	*p*-value
Model	56,609.54	5	11,321.91	1158.59	<0.0001
A-Boiling time	43,837.04	1	43,837.04	4485.94	<0.0001
B-Concentration	1282.28	1	1282.28	131.22	<0.0001
AB	360.65	1	360.65	36.91	<0.0001
A^2	11,040.01	1	11,040.01	1129.75	<0.0001
B^2	89.56	1	89.56	9.17	0.0064
Residual	205.21	21	9.77		
Lack of Fit	64.08	3	21.36	2.72	0.0746
Pure Error	141.13	18	7.84		
Cor Total	56,814.75	26			

face methodology. The estimated result of parameter and the analysis of variance (ANOVA) are presented in Table 4. P-values less than 0.5000 indicate the model terms are significant, indicating that all independent variables had a significant effect on reducing sugar yield. The value of predicted R^2 of 0.9922 is in reasonable agreement with the adjusted R^2 of 0.9944, which demonstrates the high significance of the model.

Additionally, the adequacy precision was 68.70 (not shown), showing that the model can be used to predict the optimal condition for the two-step pretreatment of coconut pulp residue. Finally, the lack of fit of the model was 0.0746, which proves that the model is significant and that the experimental data fitted the model.

The three-dimensional (3D) plot at optimum reducing sugar by sequential hydrothermal pretreatment and acid hydrolysis are shown in Fig. 2. It was observed that reducing sugars increases with a gradual change in pre-hydrothermal condition and acid concentration. This was also confirmed by the equation generated (Eq. (4)), whereas the coefficient linear term A (hydrothermal pretreatment) and B (acid concentration) possess positive sign which signifies that both independent factors can increase the reducing sugars (Manmai et al., 2020). Finally, when the results were evaluated the optimal conditions of the pre-hydrothermal treatment and acid concentration for the extraction of reducing sugar were 60 min and 3% H_2SO_4, which resulted to maximal reducing sugar yield of 120.71 g/L:

$$\begin{aligned} \textit{Reducing sugar} &= 101.13 + 44.46A + 19.90B \\ &\quad + 10.53AB - 41,53A^2 - 13.17B^2 \end{aligned} \tag{4}$$

On the other hand, the maximal reducing sugar (120.71 or 0.75 g/g) obtained in this work is comparable to other existing acid pretreated coconut pulp residue. Bujang et al. (2013) reported that the maximum sugar release from coconut pulp residue was 0.38 g/L using a 1% concentration of H_2SO_4 at 130 °C for 60 min. The resulting sugar from the optimized condition of the present study was higher due to pre-hydrothermal treatment and a higher concentration of H_2SO_4, which was found significant in the statistical analysis. On the other hand, coconut pulp residue treated with 1 M HCl at 60 °C for 30 min yields 0.099 of total sugar (glucose, xylose, arabinose), which was lower than the existing study (0.75 g/g). The reason can be drawn from this is that the present study employed H_2SO_4 rather than HCl. According to Lavarack et al. (2002), hydrochloric acid is less effective on the degradation of polymers compared to sulphuric acid. This was also supported in the study of Meinita et al. (2012), where *Kappaphycus alvarezii* (cottonii) produces higher reducing sugar with lower inhibitors on H_2SO_4 catalyst compared to HCl. In addition, the use of sulphuric acid is economically and industrially favorable since the use of hydrochloric acid is more expensive and requires equipment with greater corrosion resistance (Chen, 2015).

Meanwhile, in a study reported by Sangkharak et al. (2019), coconut meal waste sugar was pretreated with alkaline of 50% sodium hydroxide (NaOH) in 121 °C and 1 atm for 40 min followed by enzymatic hydrolysis which produced 20.3 g/L of glucose. The hemicellulose content of coconut pulp residue in this study shares higher than lignin, which is similar to the existing study. Hence, the pretreatment must be applied mainly to target the hemicellulose. The alkaline pretreatment, however, is more effective for lignin solubilization and have lesser or no effect on cellulose and hemicellulose over acid and hydrothermal process (Carvalheiro et al., 2008).

Furthermore, the method applied in the hydrolysis of coconut pulp residue was pioneering compared to other existing studies on coconut waste. In green coconut fibers, for example, pressurized pretreatment was used with the highest attainable fermentable sugar of 0.2205 g/g using pressurized dilute alkaline pretreatment (da Costa Nogueria et al., 2019). Cabral et al. (2016), reported 8.6 g/L of total reducing sugar alkaline pretreated coconut husk. Furthermore, in the study on delignification and autohydrolysis of green coconut husk, matured coconut fiber and husk, the resulting glucose was found to be in a range of 0.43–0.59 g/g (Gonçalves et al., 2015; Gonçalves et al., 2014). present study were higher compared to the latter implicating higher desirability for bioethanol production.

3.4. *Compositional analysis of pretreated coconut pulp residue*

The characterization of the liquid hydrolysate and solid residue obtained from the optimum pretreatment condition was summarized in Table 5. Liquid hydrolysate of pretreated coconut pulp residue mainly contains C5 and C6 sugars like fructose (27.93%), glucose (20.38%), and xylose (12.91%). The high amount of fructose in the liquid hydrolysate is similar to the untreated coconut pulp residue (Zheng and Li, 2018). The sugars such as xylose (12.91%), arabinose (8.53%), rhamnose (5.96%), galactose (10.64%), and mannose (1.96%) imply that the acid hydrolysis favors the saccharification of the hemicellulose. This was also confirmed with the almost 97% hemicellulose content reduction from the recovered solid residue after pretreatment.

The results of this study follow monophasic consecutive pseudo-first-order reaction, whereas xylo-oligomers present

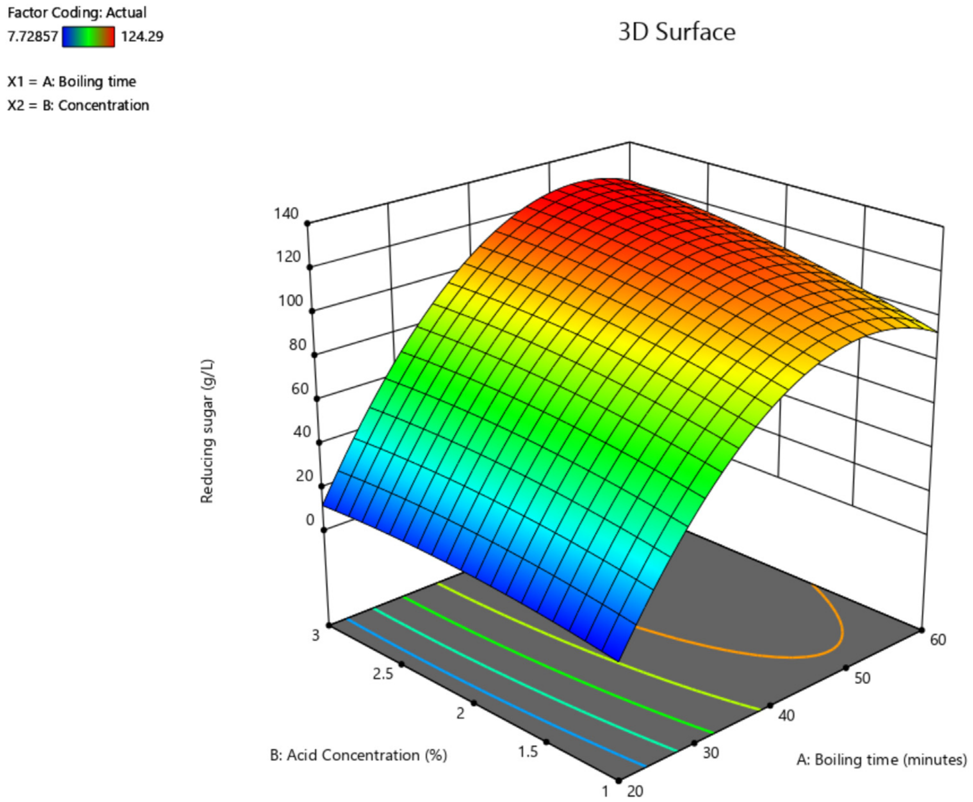

Fig. 2 – Three-dimensional (3D) response surface plots of independent variables: pre-boiling condition and acid concentration for the production of reducing sugars from coconut pulp residue.

Table 5 – Compositional analysis of liquid and solid phase of coconut pulp residue after optimum pretreatment (60 min hydrothermal pretreatment followed by 3% H_2SO_4 acid hydrolysis).

Composition	Percentage (%)
Solid phase	
Cellulose	3.32
Hemicellulose	1.50
Lignin	1.73
Liquid phase	
Mannose	1.96
Fructose	27.93
Glucose	20.38
Galactose	10.64
Arabinose	8.53
Rhamnose	5.96
Xylose	12.91
Maltotriose	4.08
Cellobiose	4.91
Citric acid	1.03
Propionic	0.60
Acetic acid	1.07
Furfural	ND
5-hydroxymethyl furfural	ND

in hemicellulose are degraded into monosaccharides when acid is introduced (Kim et al., 2013a,b). On the other hand, the glucose and cellobiose (glucose dimer) yields from the liquid hydrolysates are from the depolymerization of cellulose (Torres et al., 2017). Furfural and 5-hydroxylmethyl furfural are not detected and the amount of acetic acid (1.07%) is not severe to be considered as inhibitors for downstream fermentation (Casey et al., 2010).

On the other hand, the remaining small fractions of cellulose and hemicellulose in the solid fractions can be hydrolyzed using enzymes. The calculated degree of polymerization obtained from the optimal sugar yield was 1.2. Casabar et al. (2019) mentioned the importance of calculation of DP, whereas it represents the number of monomeric sugars in the macromolecule. The DP must be low since higher DP would eventually require intensive degradation of structural units to convert complex sugars into simple sugars like glucose. The DP achieved from the study is considered relatively low, reflecting that the sugars available in the hydrolysates are mostly reducing sugars or fermentable sugars which also signifies that coconut pulp residue was efficiently hydrolyzed by sequential hydrothermal and acid pretreatment. Overall, the sequential pretreatment enhances the sugar yield of coconut pulp residue. The reason for improvement of reducing or fermentable sugar is due to the appropriateness of the pretreatment and hydrolysis applied. The hydrothermal pretreatment partially hydrolyzed the hemicellulose into monomeric sugars and oligomers. Meanwhile, acid hydrolysis improves the release of simple sugar by further degrading the hemicellulose and oligomers into monosaccharides. The two-step treatment was effective and therefore concludes that coconut pulp residue could be an excellent feedstock for bioethanol production.

4. Conclusion

Coconut pulp residue generated after extraction of milk and oil demonstrated great potential for bioethanol production. The process for utilizing the coconut pulp residue includes two-stage pretreatment steps. Sequential hydrothermal pretreatment and post-acid treatment were carried out to the coconut pulp residue with the varying condition of pre-heating time (20, 40 and 60 min) and acid concentration (1%, 2% and 3%). Total sugar yields of 21.97, 32.47, 27.51 and 26.72 g/L were observed from 0, 20, 40 and 60 min pre-hydrothermal treatment time, respectively. Afterward, hydrothermally treated solid residues were subjected to acid pretreatment where 90% increment on reducing sugar was observed after treatment with 1%, 2% and 3% H_2SO_4 at 121 °C for 20 min. The findings also suggest the significance of the pre-boiling step as it provides sufficient reducing sugar release for bioethanol production. In addition, a combination of hydrothermal pretreatment and post-acid hydrolysis reflects a remarkable difference in reducing sugar release in comparison with alkaline pretreatment from previous studies inflicting suitability of the developed pretreatment on coconut pulp residue. The results further revealed that the optimum process condition at each stage determined through response surface methodology was 60 min hydrothermal pretreatment and post-acid pretreatment with 3% H_2SO_4 at 121 °C for 20 min. Under these conditions, the reducing sugar concentration was 120.71 g/L. Additionally, the degree of polymerization achieved in this study was low, indicating that intensive degradation or enzymatic hydrolysis is no longer required, thereby limiting the cost of biomass processing. Two-stage pretreatment design developed in this study contributed to the development of efficient bioethanol production through the generation and synthesis of high sugar from coconut pulp residue. The results of this study could benefit the ethanol industry in the sustainable supply of feedstock needed for the impending demand for bioethanol. The techniques applied in this study are simple and cost-effective; hence, a small business can produce their biofuel. Also, the results also demonstrated that most of the bio-refinery wastes could be recycled and utilized for the production of economically important products.

Conflict of interest

The authors do not have any conflict of interest for the publication of this study

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