Journal of Engineering and Sustainable Development
https://jeasd.uomustansiriyah.edu.iq/index.php/jeasd
https://doi.org/10.31272/jeasd.28.2.1

Vol. 28, No. 02, March 2024
ISSN 2520-0917

Original Research

INFLUENCE OF SUBCRITICAL WATER PRETREATMENT TEMPERATURE ON PINEAPPLE WASTE BIOGAS EFFICIENCY: EXPERIMENTAL AND KINETIC STUDY

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Received 15/11/2023 ***Revised 09/01/2024*** ***Accepted 06/02/2024***

Abstract: Anaerobic digestion of pineapple waste appears to be an effective method for non-renewable energy substitution through biogas production. The potential power generation from the exploitation of pineapple waste as fuel is estimated to be roughly 20.8 MW. Nevertheless, the intricate composition of pineapple waste, characterized by the complex arrangement of its structure, poses a significant challenge in attaining a substantial amount of biogas production. This study pretreated pineapple waste with subcritical water to increase biogas production. Two temperature settings (120°C and 200°C) were used for pretreatment. Combined pre-treatment at low temperatures and short time (120°C, 5 minutes, 10 water to solid ratio) resulted in 31.6% higher biogas production than untreated. However, pretreatment at high temperatures and longer reaction time (200°C,25 min) reduced the biogas production by 9% as compared to untreated. Using the Modified Gompertz kinetic model, pretreatment improved the lag phase and increased biogas production to 14.41 mL/day. The lignocellulosic composition of pre-treated pineapple waste decreased, while process parameters such as total ammonia nitrogen removal and pH improved after the pretreatment. Subcritical water pretreatment, particularly when conducted at high temperatures, did not yield any enhancements in the anaerobic digestion of pineapple waste. As a result, it is not advisable to employ this method for these purposes.

Keywords: *Biogas; Gompertz; pineapple waste; pretreatment; subcritical water*

1. Introduction

Pineapple is one of the Malaysian new sources of wealth with a total cultivation area of 16 thousand hectares [1]. The Malaysian pineapple market expanded to 28 million tonnes and is considered as one of Southeast Asia's leading pineapple exporters [2]. Pineapple leaves and peels are the main waste associated with pineapple commercialization, and almost a thousand tonnes of solid waste are produced

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every year. The overabundance of these wastes frequently goes untapped and is typically disposed of in landfills, leading to significant environmental issues [3]. This waste interferes with the environmental systems, contaminates the area, and raises the likelihood of spreading infectious illnesses [4,5]. One of the innovative ways to promote better waste management and utilization, particularly in rural regions, is for the waste to serve as a raw material for biogas digesters [6]. According to the Sustainable Development Goals of the United Nations, this method is an environmentally sound approach to controlling waste. The anaerobic digestion process results in the production of biogas by the breakdown of feedstock, which is assisted by a bacterial population. These processes include hydrolysis, acidogenesis, acetogenesis, and methanogenesis [7].

Pineapple wastes are susceptible to bacterial deterioration because of their water content, sugar, albumins, lipids, and vitamins [1]. Pineapple pulp has the most abundant amounts of protein and fiber when compared to other pineapple sections in terms of total protein, ash, and fibre. This waste is a suitable feedstock for the production of biogas, as it contains significant levels of carbon source as one of the known lignocellulosic wastes. According to previous research [8], the lignin, cellulose, and hemicellulose content of pineapple waste is 19.4%, 32.4%, and 23.2%, respectively. While 13.05% of pineapple leaf waste is lignin, 21.02% is hemicellulose, and 41.15% is cellulose [1]. However, high lignin content in pineapple wastes may contribute to slow microbial hydrolysis. Refractory lignin, its connection to the powerful bond between cellulose and hemicelluloses, and the existence of crystalline cellulose are all factors in the lignocellulose's strong defense against microbial degradation [9,10].

Owing to the resistant structure of the pineapple waste, the rates of anaerobic digestion of pineapple waste are constrained at the hydrolysis stage. Consequently, methane formation can be severely impacted by the inability of lignocellulosic compositions like lignin and cellulose to degrade into simple sugars [11]. The disruption of the morphological structure in lignocellulosic substrates through pretreatment has gained substantial attention as a viable strategy for biogas enhancement. Over the years, pretreatment has been commonly practiced before anaerobic digestion and various pretreatment technologies have been conducted, including thermal, chemical, biological, and combined pretreatment or its combination [12–15].

Previously, Wichitsathian et al. [16] stated that alkaline pretreated pineapple waste promotes microbial hydrolysis for subsequent anaerobic digestion and achieved over 91% and 84% of volatile solid and COD removals. Thermal pretreated pineapple waste achieved complete digestion with the domination of 70-73% acetic acid after pretreatment and produced high biogas production [17]. Besides that, acid-pretreated pineapple waste increased biogas generation by 36% and hydrogen peroxide pretreatment by 91% [18]. It also has been studied that pretreated pineapple waste helps to lower the retention time required to achieve maximum biogas production [8]. The subcritical water pretreatment technique is widely acknowledged in academic circles as a sustainable and environmentally friendly technology due to its exceptional efficacy in converting solid waste into valuable goods. The pretreatment process facilitates the disruption of structural components and enhances the accessibility of substrates subsequent to pretreatment [19]. This pretreatment involves pretreatment using water and does not require acid recycling, and is non-corrosive, non-toxic, and inflammable [14,20]. Wang et al. [9] conducted an observation and found that rice straw pretreated at a temperature of 180℃ resulted in comparatively greater cumulative biogas outputs. The author further proposed that this pretreatment enhances the biogas production. Furthermore, it has been observed that pretreatment temperatures below 150℃ have the effect of enhancing the hydrolysis of organic matter and facilitating its breakdown in the context of anaerobic digestion. To date, limited studies are available detailing the performance of subcritical water pretreatment on the biogas production and kinetics using pineapple waste as feedstock. Previous study highlights that at high temperature (>200℃), the biogas production began to drop [21]. However, detailed information on the effect of high and low subcritical water temperature on biogas production has not yet been discussed. The absence of this information significantly limits the knowledge on the effectiveness of the subcritical water pretreatment. It is crucial to explore the effect of these pretreatment temperatures on the lignocellulosic structural changes that are responsible for subsequent biogas enhancement. So far, there has been a lack of investigation into the potential impact of pretreatment on important anaerobic digestion parameters. Kinetic studies have been employed to simulate anaerobic digestion, a process of significant importance in optimizing, forecasting, modeling, and monitoring process performance across many scenarios. Several kinetic models have been used to evaluate biogas production [9,11,22,23], but none have been used for subcritical water-pretreated pineapple waste to the authors' knowledge.

Hence, the primary objective of this study is to examine the efficacy of subcritical water pretreatment in enhancing biogas production from pineapple wastes, both at low (120℃) and high temperature (200℃) conditions. Additionally, the study seeks to analyze the impact of subcritical water pretreatment on the composition of the treated pineapple waste. Furthermore, the study aims to identify any differences in the parameters and kinetics of the anaerobic digestion process resulting from the pretreatment.

2. Materials and Methods

2.1. Sample Preparation

Pineapple waste was obtained from Pasar Borong Selangor, Malaysia. Pineapple waste consisting of pulp, core, peel, and crown was mixed together with equal parts of water and blended using an electrical blender (Panasonic MX-GM1011, Japan). Then, it was screened using 1 mm screens (Retsch, Germany) to remove the water. The solid part was used as the substrate and was kept and chilled at 4 °C until it was used. Fresh manure that had been digested in anaerobic conditions for more than a month was used as the inoculum source. Before beginning the batch test, the inoculums were acclimatized in a water bath at a mesophilic temperature to allow the microbes to grow.

2.2. Subcritical Water Pretreatment

The subcritical water pretreatment was carried out in an oil bath unit that was made up of a high-temperature reaction bath with a stirrer to maintain a homogeneous fluid (Fig. 1). Silicone oil (Systerm Chemicals) was used as a heating medium as it is suitable for reactions ranging from 100℃ to 250℃ [24]. The pineapple waste mixture was poured into a 30 mL steel reactor (Swagelok Company, Japan). The subcritical water pretreatment was conducted at

120ºC and 200ºC (low and high temperature) based on Table 1.

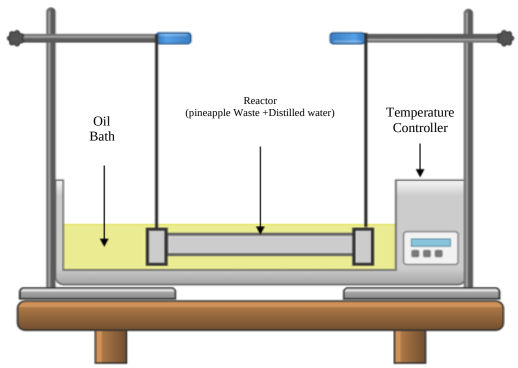


Figure 1. Subcritical water pre-treatment setup

Five grams of pineapple waste were measured and transferred to the reactor, along with 20 milliliters of distilled water, to obtain the final working capacity of 25 milliliters. Before assembly, the reactor head was tightened after argon gas was purged for 1 minute. The oil was pre-heated to achieve the desired temperature before each pretreatment. The reactor was submerged in an oil bath via a steel basket. After a specific amount of time, the reactor was removed from the oil bath and rapidly cooled to ambient temperature by submerging it in cold water. To lower the pressure inside, the pretreated pineapple wastes were allowed to undergo a cooling process inside the reactor prior to getting removed.

Table 1. List of subcritical water pretreatment conducted before anaerobic digestion.

Run	Temperature (°C)	W/S ratio* -	Time (min)
1	120	10	5
2	120	10	25
3	120	5	5
4	120	5	25
5	200	10	5
6	200	10	25
7	200	5	5
8	200	5	25

*Water to Solid ratio

2.3. Anaerobic Digestion Set-Up

The experimental procedure involved conducting batch digestion of pineapple wastes that had been pretreated with subcritical water. This process was carried out in 125 mL serum bottles, maintaining a mesophilic temperature. The working volume was 100 mL, and the concentration of the substrate used was 30 gVS/L, as per the method described by Hamzah et al. [22]. The untreated (UT) pineapple waste was used as the blank sample. The inoculum was combined with a 25 mL mixture of substrate to achieve a working volume of 100 mL. The serum bottles used for the anaerobic digestion assays were capped with an aluminum cap and a rubber stopper (Fig. 2). The bottles were submerged in water, which was kept at 37±1°C in a water bath (Memmert, Germany). Using either sodium hydroxide or hydrochloric acid, the substrate's pH was brought to 7. After that, the serum bottles were capped with an aluminium cap following a 2-minute exposure to nitrogen gas purging to remove excess oxygen. Up till the plateau of generated gas, batch testing was conducted for 40 days and it was done in triplicate for each batch test. Daily measurements were made of the gas production. The substrates were shaken prior to the gas collection each day and immersed to a height of half their height. Fig. 1 illustrates the water displacement technique employed to determine the total amount of the gas generated. A carbon dioxide scrubbing unit was employed to eliminate any residual traces of carbon dioxide in the gas. The scrubber contained 3 M sodium hydroxide solution.

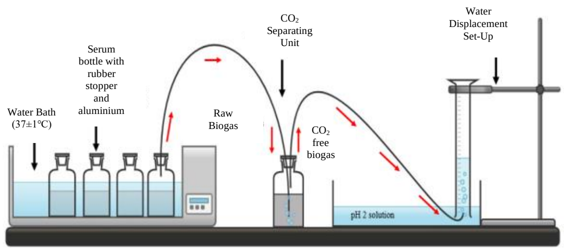


Figure 2. Anaerobic digestion set-up

2.4. Analytical Methods

Before pretreatment and the anaerobic digestion procedure, the pineapple was initially characterized. The standard method for the examination of water and wastewater served as the basis to determine the TS, VS, and TAN [25]. The TAN measurements were carried out in accordance with standard procedure #4500-D. The CHN628 Series (LECO, United States) was used to analyze the C and N contents, and the results were used to calculate the substrates' C/N ratio. A pH meter was used to measure the pH value (pH5SS Spear pH Tester, IONIX, Singapore). Based on the Technical Association of the Pulp and Paper Industry (TAPPI) standard procedures, the percentage of lignin, cellulose, and hemicellulose in pineapple waste was determined [26]. T-222 was used to determine the amount of lignin. Following the T-249-75, the holocellulose was identified. The amount of α-cellulose was determined using T-203. Three replications of each characterization were made. The methane composition present in the biogas produced on the 10th day of the digestion was analyzed using gas chromatography with a thermal conductivity detector instrument (Agilent 6890 N, United States).

2.5. Kinetic Study

Using the Modified Gompertz model equation, the cumulative biogas production data was kinetically examined. Numerous crucial data for the anaerobic digestion process are provided by the kinetic study, including the lag phase and the maximal biogas production rate. In this study, the modified Gompertz equation (Eq. 1) was employed to elucidate the behavior and process of anaerobic digestion [22].

$$B = B_0 \exp\left\{-\exp\left[\frac{\mu.e}{B_0}(\lambda - t) + 1\right]\right\} \qquad (1)$$

where B is biogas production yield (mL/g VS), B_0 is the maximum biogas yield (mL/g VS), μ is the maximum biogas production rate (mL/g VS.day), e is exp (1), λ is the lag phase period and e is an Euler's function with a value of 2.71828. The solver tool in Microsoft Excel was employed to compute the kinetics constants B, B_0, and λ.

3. Results and Discussion

3.1. Samples Characterization

The characterization processes that were carried out on the substrates utilized in the tests are listed in Table 2. The pineapple waste used in this experiment displays a high moisture content that is similar to the pineapple waste that was used by Wichitsathian et al. [16] in their study. Furthermore, it is clear that the VS of the pineapple waste used in this study is a little higher. VS represents the fraction of biodegradable material that is susceptible to being degraded [22]. The high VS content shows that there is a higher amount of organic matter in the pineapple waste, which would increase the degradation rate.

Table 2. Characteristic of pineapple waste inoculum used in this study.

Characteristic	Pineapple Waste	Inoculum
TS (%)	5.37±0.25	2.59±0.08
MC (%)	94.63±0.25	97.41±0.08
VS (%)	93.42±0.45	74.38±0.62
Ash (%)	6.58±0.45	25.60±0.59
pH	4.51±0.03	7.45±0.02
C (%)	43.71±0.18	-
H (%)	6.49±0.06	-
N (%)	1.22±0.06	-
C/N	35.91±1.62	-
TAN (mg/L)	-	-
Lignin (%)	13.22±0.11	-
Cellulose (%)	41.85±0.87	-
Hemicellulose (%)	36.20±0.54	-
Extractives (%)	8.73±0.43	-

-Data not available

Apart from being rich in organic matter, pineapple waste also contains a large amount of natural carbohydrates, with cellulose making up the majority (41.8%), followed by lignin (13.2%) and hemicellulose (35.2%). The lignin content in this study is low compared to the literatures [8,16]. Since lignin is resistant to microbial attack and hard to break down, substrates with lower lignin percentages are preferred as a digestion substrate. The fact that pineapple waste has a greater C/N ratio further supports the idea that it can act as a good carbon source for the microbes involved in the anaerobic digestion process. The pH of the substrates was corrected to 7 before the experiment began because, in accordance with the literature, the pH of pineapple waste is not ideal for the process of anaerobic digestion [22]. A VS of 74.38%, pH of 7.45, and TS of 2.59% were present in the inoculum used in this study.

3.2. Biogas Production

The effect of subcritical water pretreatment temperatures on pineapple waste was studied, and is shown in Fig. 3. According to Fig. 3a, the biogas production of low-temperature sets achieved a significant peak between 2 to 5 days after digestion started, with volume ranging from 12 mL to 20 mL per day which equivalent to 4 mL/ gVS to 7.33 mL/g VS of biogas yield respectively. The quick breakdown of the readily soluble components in pineapple waste may be the cause of the untreated pineapple waste's biogas generation, which swiftly peaked on the 1st and 2nd day and then gradually reduced until the digestion period ends. These trends are similar to those reported by He et al. [23], who they also observed that untreated wheat straw produced the first peak on the first day of the digestion period. Compared to untreated, run 1 to 4 still produced a peak after the 5th day, the continuous peak observed may have been caused by changes in the lignocellulosic structure of pineapple waste due to the subcritical water pretreatment which also appears to promote the anaerobic digestion process [27].

The 1st daily biogas production of high-temperature samples at 200ºC showed poor performance as compared to the untreated pineapple waste.

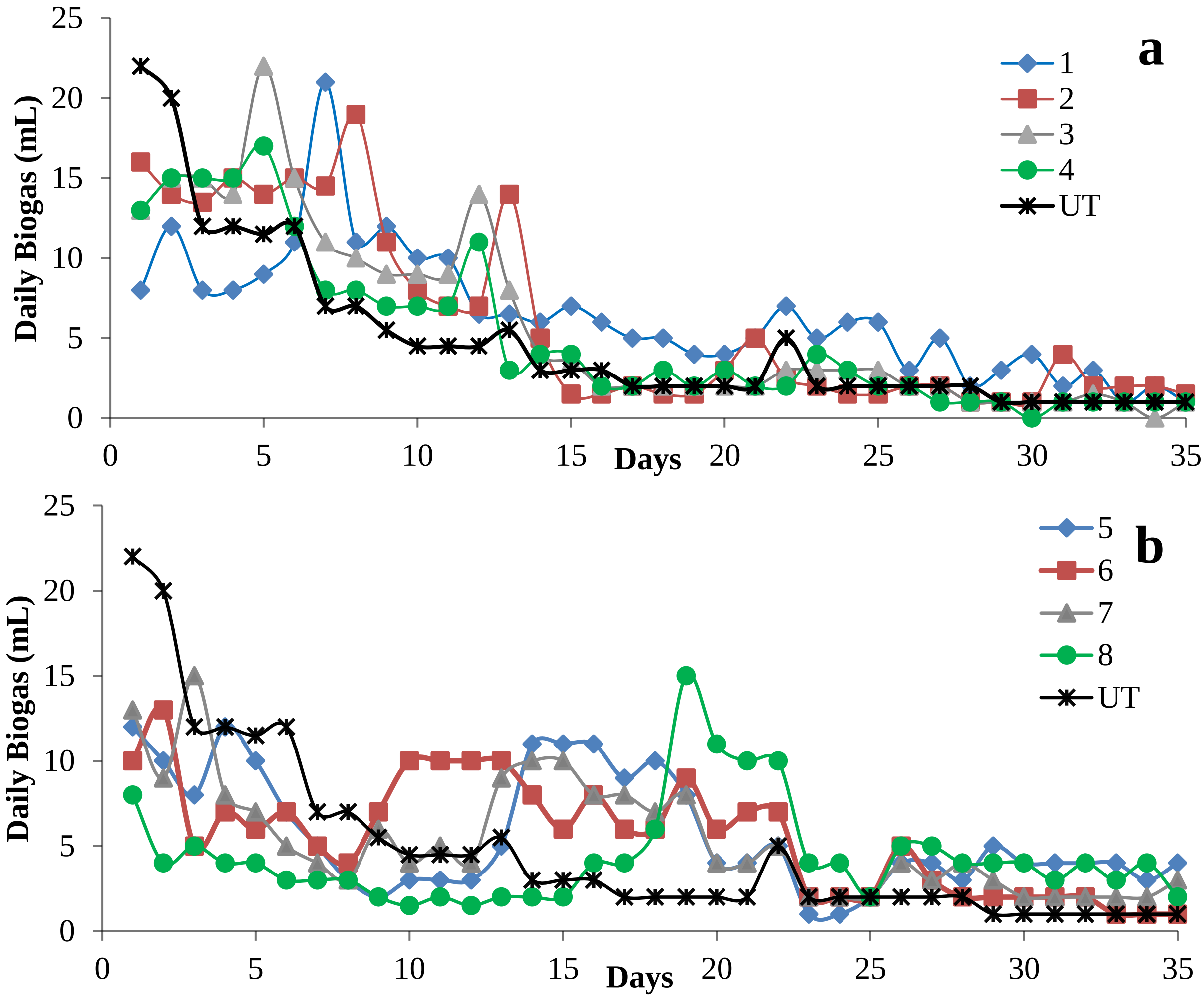


Figure. 3 Daily biogas production of (a) low temperature (120ºC) and (b) high temperature (200ºC) of subcritical water pretreated and untreated pineapple waste

As shown in Fig. 3b, daily biogas production during the first 8 days of the digestion period is lower than untreated. The duration of the subsequent peaks, however, clearly differed from low-temperature samples. The following biogas peak of run 6 occurred after the 13th day of the digestion period. The peak was prolonged to the 13th day for run 7 and 14th day for run 5, and even to the 19th day for run 8. Similarly, Xiang et al. [28] experienced a delay in biogas production of rice straw at high temperature, temperature more than 180°C produced 2nd peak after the 14th to 15th day after digestion. These findings align with He et al. [7], Wang et al. [19], and Xiang et al. [24], which authors mention that raising the pretreatment temperature would have a negative impact on the biogas productivity, specifically at temperatures above 200°C, high possibility due to the anaerobic medium becoming acidic due to the formation of soluble compounds during high-temperature pretreatment, particularly compounds that were produced from the structural components.

Based on Fig. 4, the cumulative biogas production facilitated by subcritical water pretreatment, and the relatively higher cumulative biogas production were correspondingly achieved by Run 1 at 225 mL which is equivalent to 75 ml/g VS biogas yield, respectively, followed by Run 2 (215 mL), but over the entire digestion period, run 8 produced only 155 mL of biogas. Nevertheless, subjecting the waste to a temperature of 200℃ for a prolonged duration of 25 minutes at a water-to-solid ratio of 5, resulted in a decrease in biogas by 9%. Compared to untreated pineapple waste, run 1 at a temperature of 120℃ increased biogas production by 31.6 %, whereas Run 5 at a temperature of 200℃ only increased it by 13.5%. Likewise, rice straw pretreated at 120℃ promotes biogas yield 34% higher than untreated while, at higher temperatures, biogas production was increased only at 19% [28]. It can be observed also in Fig. 4 that although improvement can be observed at the subcritical pretreated sample, however at low pretreatment temperature (Run 1- 4) varying reaction time and the solid-to-water ratio does not give significant changes to biogas production. The same trends can be observed at high temperature of 200℃ samples (Run 5 to 8). This explains that reaction time and solid-to-water ratio do not affect the biogas production from subcritical water pretreated pineapple waste.

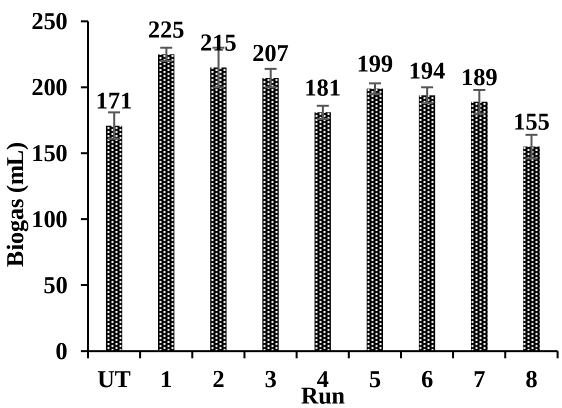


Figure. 4 Cumulative biogas production of subcritical water pretreated and untreated pineapple waste.

Previously, Park et al. [21] observed that the reaction time of biogas produced at temperature 125 to 200℃ is not significant and does not have an effect on biogas production. Also, Aili Hamzah et al. [20] also explained that only the temperature of subcritical water pretreatment produces a highly significant effect on biogas yield as compared to water to solid ratio. Given that increasing the subcritical water temperature does not increase anaerobic digestion, it is not advised to conduct subcritical water pretreatment for the anaerobic digestion process specifically at temperatures greater than 200 ℃. The Maillard reaction leads to the production of recalcitrant compounds and changes in the substrate's properties, resulting in nutritional loss that could inhibit methanogenesis [7,29]. This affects the biodegradation and the biogas formation, resulting in a decrease in biogas yield [30,31]

3.3. Compositional Analysis

Fig. 5 shows the changes in the composition of lignin, cellulose, hemicellulose, and also extractives in subcritical water pretreated pineapple wastes and untreated samples. The highest lignin reduction was observed in Run 1 which dropped from 13.22% to 11.98% as compared to untreated. Delignification of pretreated samples had taken place, as evidenced by the drop in lignin content. Meanwhile, the highest cellulose content was shown by pretreated samples at 200℃ temperature settings. What can be seen in Fig. 5 is that the hemicellulose reduction can be detected in the pretreated samples. The hemicellulose fraction in the pretreated sample was 37.23%, which is 2.85% higher in Run 7 than in untreated samples. It also can be observed that the lignin content of subcritical water-pretreated pineapple waste increases at high temperatures (200℃). The main cause of the increments in lignin composition was not due to the increase in lignin percentage but rather due to alterations of cellulose and hemicellulose in the whole composition. This finding is supported by Antwi et al. [14] and Wang et al. [9], where both of the authors observed an increase in lignin content when increasing the pretreatment temperature. Furthermore, this pattern is often shown through numerous studies involving the utilization of both softwood and hardwood waste. These studies operated under the assumption that subjecting the wastes to subcritical water pretreatments could result in the conversion of certain cellulose and hemicellulose components into pseudo-lignin. This pseudo lignin is known to contribute to the augmentation of acid-insoluble lignin levels [32,33]. In the present study, an increase in the cellulose content within the pretreated pineapple sample resulted in alterations to the crystalline cellulose structure, rendering it more susceptible to microbial degradation [10]. Hemicellulose concentration in the solid portion of the pretreated waste was lower, indicating that the predominance of hemicelluloses was present in the liquid part of the pretreated sample and a high portion of hemicelluloses were solubilized from the solid fraction [34]. The breakdown of pineapple wastes' lignocellulosic composition under subcritical water conditions, in which the pretreatment altered the waste's structure to allow methanogens have better to access it for better biogas production.

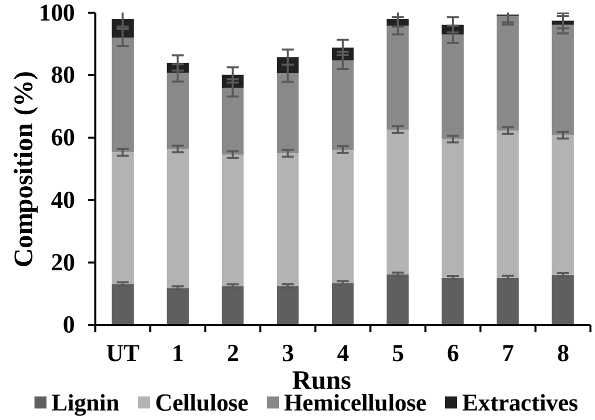


Figure 5 Pre- and post-subcritical water pretreatment compositional characterization.

3.4. Process Parameters

The initial and final effluent on anaerobic digestion of subcritical water pretreated pineapple waste process were evaluated. Table 3 summarizes the pH, VS removal, and TAN. It can be seen that no drop in pH from the initial pH of 7. This confirms that no inhibition occurred by rapid acidogenesis using a pretreated sample that could contribute to the pH drop low and biogas production [29]. The final effluents can rise to 7.28, and it was determined that none of the end pH values of the pretreated pineapple waste differs greatly from the starting pH of 7.

Table 3. Summary of results of anaerobic digestate effluents of subcritical water pretreated pineapple waste.

Run	Parameters			
	pH	**VS Removal (%)**	**Initial TAN (mg/L)**	**Final TAN (mg/L)**
UT	7.28 ± 0.04	40.96 ± 4.56	129.73 ± 3.23	557.2 ± 24.25
1	7.09 ± 0.02	77.17 ± 1.61	46.2 ± 9.9	389.2 ± 7.92
2	7.16 ± 9.03	52.1 ± 4.23	32.2 ± 9.9	728 ± 11.88
3	7.18 ± 0.03	71.31 ± 1.66	44.8 ± 7.92	194.6 ± 9.9
4	7.21 ± 0.04	54.81 ± 3.17	50.4 ± 9.9	512.4 ± 11.88
5	7.15 ± 0.01	56.03 ± 4.47	57.4 ± 1.98	173.6 ± 7.92
6	7.27 ± 0.02	52.34 ± 2.13	42 ± 3.96	193.2 ± 7.92
7	7.13 ± 0.01	64.18 ± 1.37	37.8 ± 5.94	476 ± 15.84
8	7.24 ± 0.02	73.32 ± 1.44	54.6 ± 5.94	218.4 ± 7.92

In a study of pretreated rape straw, the pH value in all digesters was reported within the range of 7.50 to 7.63 [35]. The maximum pH reported was higher than in the present study. Similarly, Tian et al. [36] stated that the hydrothermal pretreated wheat straw and waste-activated sludge recovered faster when treated and achieved the suitable pH for methanogens ranging from 6.8 to 7.2. The final TAN levels in the effluents were between 173.60 to 728 mg/L. TAN inhibition did not occur in this study as the highest TAN concentration did not beyond the level of inhibition. Low biogas production often results from TAN level increased over the threshold value which inhibits methanogenic activity [37]. Previously, hydrothermal subcritical water pretreated sewage sludge reported higher TAN levels of 614 to 817 mg/L.

According to the authors, the TAN concentration increased under subcritical water conditions. However, operating the pretreatment under 175 ⁰C produced a lower TAN concentration and reduced TAN inhibition risk [21]. Other than that, Gaballah et al. [35] reported that no TAN inhibition occurred when pretreatments were applied to rape straw (673.2 mg/L to 748.1 mg/L). The highest VS removal from the subcritical water-pretreated pineapple waste was observed at 77.17 %. The lowest VS removal was reported in the untreated sample for only 40.96% of VS removal. Previously, Dahunsi [8] reported 38% of VS removal from H_2SO_4 pretreated pineapple waste and 53% of VS removal from H_2O_2 pretreated pineapple waste. Higher VS removal reported by Gaballah et al. [35], rape straw pretreated with the steam explosion at 180 °C combined with grinding resulted in 71.2 % VS removal followed by dilute acid followed and steam explosion at 190 °C with 70.6% VS removal. High VS removal reported in this study (77.17%) proved that subcritical water pretreatment helps to convert a substantial quantity of biodegradable material into biogas.

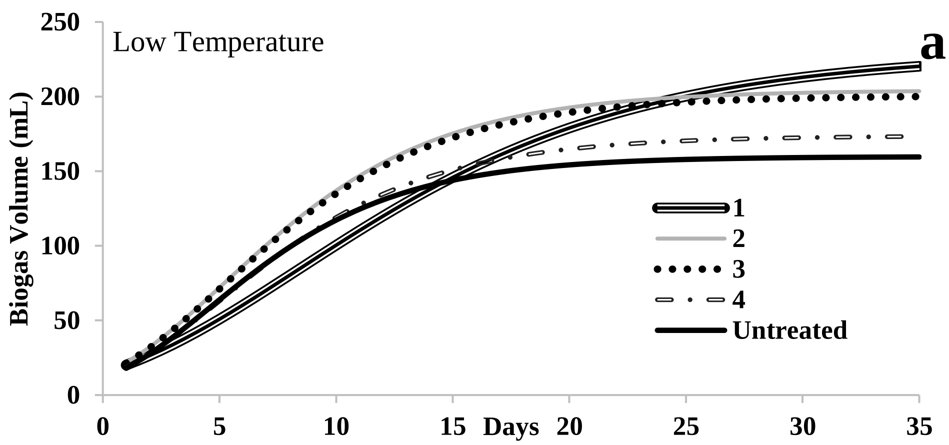
3.5. Kinetic Study

It is assumed by the modified Gompertz model equation (MGM) that the rate of biogas production in the digester is directly proportional to the rate at which methanogenic microbes grow. It can be seen in Fig 6a, that runs 2 and 3 Produced faster biogas production compared to untreated while the slowest production can be seen at Run 8. It can be concluded that at low temperatures the microbial growth rate is faster than untreated and at 200℃, the microbial growth rate is slower in all runs as compared to untreated samples. Table 4 summarizes the predicted parameters of the MGM's equation. Among all of the pretreated samples, run 7 showed the lowest deviation (0.69%) between the measured and predicted biogas production followed by Run 6 (1.17%) Run 2 showed the highest deviation between the measured and predicted biogas production (5.59%). The variation between the actual and predicted data must be below 25% to achieve optimal accuracy in the analysis, fitting, and prediction of biogas production. However, it was indicated that there is negligible variance (below 10%) should be taken into account to foresee the biogas production precisely [22].

Low λ was recorded for low-temperature subcritical water pretreated pineapple waste and high λ was observed at the highest and longest pretreatment temperature and reaction time (200℃ for 25 minutes). An increase in the amount of α-cellulose after pretreatment increases the λ. Thus, the increasing amount of cellulose in pretreated pineapple waste increases the number of substrates to digest. The more the number of available substrates added, the prolonged duration is required for the bacteria to break the substrates down as a result of its intricate composition. Similarly, the λ of the solid fraction hydrothermal subcritical water pretreated rice straw increased from 3.49 to 5.25 days [28], a slight increase in λ from 3.23 to 3.45 and 3.79 observed by fungal pretreatment of rice straw [38] and λ increase from 1 day to maximum of 9.9 using acid and alkali pretreatment for tobacco stalk [11].

The maximum biogas production rate (μ) showed an increasing trend for the lower subcritical water pretreatment temperature. Conversely, increasing subcritical water pretreatment temperature decreases the μ. The highest μ was observed at run 2 with 14.41 mL/g VS.day and the lowest was at run 8 with only 5.46 mL/g VS.day. The regression coefficient (R^2) values are derived from the analysis of variance[39]. The R^2 for the biogas production from the pretreated pineapple waste is also higher in comparison with untreated materials.

Thus, the anaerobic digestion of pretreated pineapple waste demonstrated a high level of accuracy and consistency between the experimental findings and model prediction. The study also demonstrated a significant relationship between the kinetic model and the actual biogas production, as evidenced by the high R^2 values approaching 1. Previously, a good relationship between model prediction and experimental findings was observed anaerobic digestion of microbial pretreated water hyacinth where R^2 from 0.91 to 0.95 after pretreatment was applied [12]. The R^2 for biogas production from chemically pretreated agricultural waste and animal manure was reported at a range of 0.979 to 0.994 using a modified Gompertz model [40], while hydrothermal subcritical water pretreated rice straw reported an R^2 increase from 0.9944 to 0.9989 after pretreated at a subcritical water temperature of 150 ºC [9].



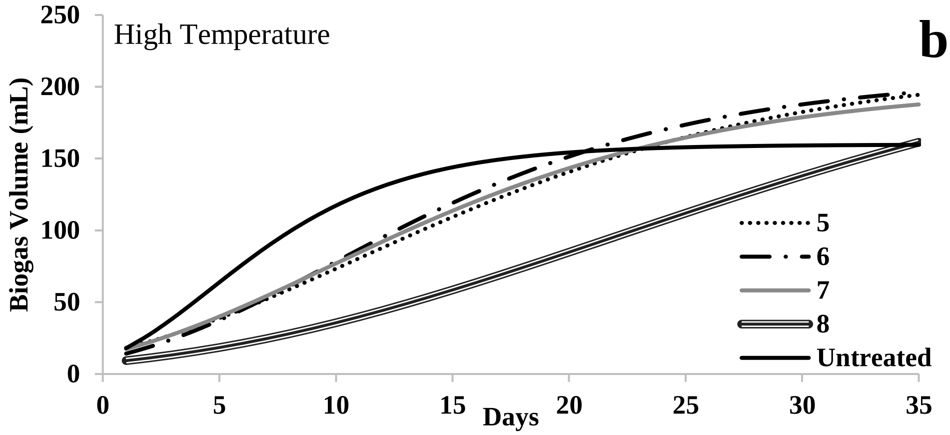


Figure 6 Comparison of biogas production of subcritical water pretreated pineapple waste using Modified Gompertz model equation (a) Low temperature (120ºC) (b) High temperature (200ºC).

Table 4. Kinetic parameters of biogas production during anaerobic digestion - the Modified Gompertz model.

Run	Experimental Biogas (mL)	Predicted Biogas (mL)	Methane Content (%)	λ (day)	μ (mL/d)	B_0 (mL)	R^2	Dev
Untreated	171	159.56	71.72	0.0	12.77	159.78	0.9619	7.17
1	225	220.29	87.61	0.1	10.14	229.53	0.9921	2.14
2	215	203.61	85.44	0.0	14.41	204.29	0.9917	5.59
3	207	200.01	85.14	0.0	14.21	200.66	0.9917	3.49
4	181	173.29	88.55	0.0	12.61	173.76	0.9861	4.45
5	199	194.43	84.97	0.0	7.33	216.82	0.9878	2.35
6	194	196.30	87.56	0.9	8.59	208.31	0.9980	1.17
7	189	187.70	83.50	0.0	7.70	201.74	0.9928	0.69
8	155	161.37	80.03	4.5	5.46	257.83	0.9816	3.95

Notes: λ lag phase period, μ the maximum biogas production rate, R^2 correlation coefficient.

4. Conclusions

This study investigated low- and high-temperature subcritical water treatments on pineapple waste. Biogas production was higher with low temperature (120℃) subcritical water pretreatment compared to high temperature (200℃). In Run 1 (120℃, 15 minutes, 10% water to solid ratio), biogas production reached 225 mL, resulting in 75 mL/g VS biogas yield and a 31.6% increase over untreated pineapple. Run 1 using subcritical water pretreatment had the highest lignin reduction (11.98%) together with high biogas production. Lignin affects the production of biogas more than cellulose and hemicellulose. Subcritical water pretreatment enhanced anaerobic digestion VS removal, final TAN, and pH. Cumulative biogas production was analyzed by a modified Gompertz kinetic equation fitted with the experiment and predicted value. Longer λ at 200°C suggests more degradable substrates formed after pretreatments. Our research gives important information and potential ways for effectively utilizing pineapple waste, especially in an environmentally friendly manner, and generating cleaner bioenergy.

Acknowledgments

The research conducted in this paper received financial support from the Scheme of the Malaysian Ministry of Higher Education (Ref. No. FRGS/1/2021/TK0/UPM/02/28).
The authors would like to express their gratitude for the assistance and technical resources provided by the Department of Biological and Agricultural Engineering, Department of Chemical and Environmental Engineering, Smart Farming Technology Research Centre, and Faculty of Engineering, Universiti Putra Malaysia.

Abbreviations

B_0	Maximum biogas yield
R^2	Regression coefficient
TAN	Total ammonia nitrogen
TS	Total solid
VS	Volatile solid
μ	Maximum biogas rate
λ	Lag phase

Conflict of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

Author Contribution Statement

Conceptualization, Adila Fazliyana Aili Hamzah; Muhammad Hazwan Hamzah and Hasfalina Che Man; Formal analysis, Adila Fazliyana Aili Hamzah; Investigation, Adila Fazliyana Aili Hamzah; Methodology, Adila Fazliyana Aili Hamzah; Muhammad Hazwan Hamzah; Nur Syakina Jamali and Shamsul Izhari Siajam; Supervision, Muhammad Hazwan Hamzah; Hasfalina Che Man; Nur Syakina Jamali and Shamsul Izhar Siajam; Validation, Muhammad Hazwan Hamzah; Hasfalina Che Man and Nur Syakina Jamali; Writing—original draft, Adila Fazliyana Aili Hamzah and Muhammad Hazwan Hamzah; Writing—review and editing, Hasfalina Che Man; Nur Syakina Jamali and Shamsul Izhar Siajam. All authors have read and agreed to the published version of the manuscript.

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