The effect of pretreatment methods for improved biogas production from oil-palm empty fruit bunches (EFB): experimental and model

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Abstract. The production of biogas from solid wastes in addition to palm oil mill effluents is necessary due to the shortage of the effluents, operation of biogas plants at low to moderate capacities, and large amount of solid wastes, particularly oil-palm empty fruit bunches (EFB). However, the biogas production from raw EFB gives low yield. This study therefore aims to investigate the effect of EFB pretreatment methods on the improvement of biogas production. The pretreatment of EFB was carried out through chemical (NaOH solutions), physical (size reduction) and biological (activated sludge and bio-scrubber effluent) processes. The experimental data was tested against corrected Gompertz model. The results showed that size reduction and pretreatments of EFB with 7% w/v NaOH, activated sludge and bio-scrubber effluent could improve biogas yield significantly and differently. The highest yield of methane was 429.9 ml/g.VS, obtained from EFB with size reduction. For the pretreatments of EFB with 7% w/v NaOH, bio-scrubber effluent and activated sludge, the methane yields were 345.5, 326.4 and 297.3 ml/g.VS, respectively. Without pretreatment, the methane yield was only 226.0 ml/g.VS. The change in cellulose and lignin compositions of EFB after pretreatment is attributed to the improvement of biogas yield. It is economically interesting that the bio-scrubber effluent from palm oil mills can be recycled to treat EFB. In the modeling study, the corrected Gompertz model could fit all data sets reasonably well.

Keywords: Pretreatment method, Empty fruit bunches, Biogas production, Gompertz model.

1. Introduction
The development of alternative energy in Thailand has been consistently increasing due to the governmental policy that strongly supports this type of energy. Biogas is promising alternative energy since Thailand is an agricultural country generating various forms of residues that can be used as raw materials for biogas production. However, most of the agricultural residues are in solid state containing cellulose, hemicellulose, and lignin. This firm molecular structure is unable to be digested easily. As a result, the biogas industry is currently deprived of raw materials. According to the statistics, Thailand has more than 14 million tons of oil palm bunches per year [1], which generates about 2.8 million tons
of oil palm empty fruit bunches (EFB) annually. Therefore, EFB is a promising raw material used for the production of biogas.

The structure of EFB contains 41.3-45.0% cellulose, 25.3-33.8% hemicellulose, and 27.6-32.5% lignin [2-4]. In biogas production, the efficiency of degradation greatly depends on the amount of lignocellulose components. The pretreatment of EFB before the biogas production process was found to significantly enhance the methane yield compared to non-treated EFB [4]. There are several pretreatment methods to improve the biodegradability of lignocellulosic materials by opening up their compact structure [5]. They could be classified into physical, chemical and biological methods. Physical method mostly involves the application of mechanical strength to substrates for the purpose of size reduction. This method generates no inhibitors and usually increase methane production. However, the physical method requires energy. Chemical pretreatment method is simple and does not require much energy compared to physical method. Without pretreatment the yield of methane from EFB was 358 ml/g.VS [6]. The methane yield increased to 404 ml/g.VS when EFB was pretreated with 8% NaOH [7]. The disadvantage of chemical pretreatment, however, is the requirement of pH adjustment to be neutral after the pretreatment step. Biological pretreatment method typically uses enzymes or microbes to digest lignin and hemicellulose components while cellulose is slightly digested. This method uses less energy and no chemicals. However, the operation needs to be controlled carefully.

This research aims to study the effects of the different pretreatment methods of EFB on biogas production. EFB was pretreated with chemical (NaOH solution), physical (size reduction), and biological (bio-scrubber effluent and activated sludge, AS) methods. Kinetic model based on corrected Gompertz model was proposed in order to explain the biogas production from EFB.

2. Materials and methods

2.1. Characterization of Substrates and Inoculum

EFB was acquired from EFB shredders in a palm-oil mill in Thailand. Prior to use, EFB was kept in a closed container avoiding the contact of sunlight and humidity. Total solid (TS) and volatile solid (VS) contents of EFB were analyzed according to standard methods for the examination of water and wastewater (APHA) [8]. The inoculum of methanogenic bacteria was obtained from an anaerobic sludge at the bottom of an anaerobic pond in a palm-oil mill. The inoculum was capable of producing methane as confirmed by the Specific Methanogenic Activity (SMA): 0.2631 g CH4-COD/g VSS/day. Prior to use, the inoculum was left at 55 °C for 3 days in order to completely consume the residual nutrients.

The pretreatment of EFB was classified as: (i) physical (size reduction); (ii) chemical (NaOH solutions at three different concentrations); (iii) biological (bio-scrubber and AS). After the pretreatment, the remaining EFB was washed with water several times until neutral pH was obtained. It was then analyzed based on the compositions of lignin [9], hemicellulose and cellulose [10]. The carbohydrates and reducing sugar content were also determined using the AOAC method [9].

2.2. Biochemical Methane Potential (BMP) Experiment

The methane production from EFB after pretreatment was carried out in a batch mode under high solid anaerobic digestion (10-15 %TS). The 500-ml serum bottles were used as digesters in all experiments. The bottles were covered with air-tight caps. Oxygen was first removed by flushing the bottle headspace with nitrogen gas. The temperature was kept constant at 55 °C in an incubator. Digestion was continued up to 35 days. The volume of biogas was measured daily using a water displacement method. At the end of the digestion process, the composition of the biogas was measured with an automatic biogas analyzer (GFM 416, GasData). All experiments were carried out in triplicate manners. Five different operating conditions were used for biogas production: (i) 10 g of EFB without pretreatment (average size = 3 cm) (ii) 10 g of EFB after size reduction (average size = 0.5 cm); (iii) 10 g of EFB after pretreatment with 3-7% w/v NaOH; (iv) 10 g of EFB after pretreatment with bio-scrubber effluent; (v) 10 g of EFB after pretreatment with AS. All experiments were identically loaded with 160 g of inoculum. For control experiment, only 160 g of inoculum was loaded without substrate.
2.3. Kinetic Models of Biogas Production

Siripatana reformulates Schnute postulation and proposed the corrected form of Gompertz equation as discussed below [11]. The original form of Gompertz model is shown in Equation (1).

\[ P = P_e' - \beta_0 \left[ \exp \left( -x/\beta \right) \exp \left( -\mu/\alpha \right) \right] - \exp \left( -x/\beta \right) \]

A modified form of Gompertz model is presented in Equation (2).

\[ \left( P + P_e' \right)/\left( P_e + P_e' \right) = \exp \left( \left( R_m e/\left( P_e + P_e' \right) \right) \left( \lambda - 1 \right) + 1 \right) \]

and

\[ \lambda = \alpha^{-1} \ln(\delta - 1), \quad R_m = \left( P_e + P_e' \right) \alpha/\gamma, \quad \alpha = R_m e/\left( P_e + P_e' \right) \text{ and } \delta = 1 + \exp(\lambda \alpha) \]  

It seems that this corrected form now has four parameters instead of three. In fact, the independent parameters of the corrected Gompertz model are still three since \( P_0 \) is related to \( P_e \) by Equation (4).

\[ P_e' = \left( P_e + P_e' \right) \exp \left( \left( R_m e/\left( P_e + P_e' \right) \right) \lambda + 1 \right) \]  

Unfortunately, Equation (4) is not explicit in either \( P_0 \) or \( P_e \). It is recommended that the original form of Gompertz equation should be used. If \( R_m \) and \( \lambda \) are required, it can be calculated by Equation (3).

According to the authors’ opinion, the corrected form of the modified Gompertz model (Equation (2)) as developed by Siripatana is parsimonious and should be used for representing normal accumulative biogas evolution (ABE) curves obtained from batch anaerobic digestion experiments. All four parameters have direct physical/biological meaning and are easily estimated by non-linear regression software available today.

3. Results and discussion

3.1. Effect of pretreatment on EFB structures

The composition of EFB samples after pretreatment with different methods was analyzed based on TS and VS contents, concentrations of reducing sugar and carbohydrates, and the compositions of cellulose, hemicellulose and lignin as shown in Table 1.

Table 1. Properties of EFB samples after pretreatment with different methods compared to untreated EFB

| Methods                  | Reducing sugar (g/l) | Carbohydrates (g/l) | Cellulose (%) | Hemicellulose (%) | Lignin (%) | TS (g/kg) | VS (g/kg) | VS/TS (%) |
|--------------------------|----------------------|---------------------|---------------|------------------|------------|-----------|-----------|-----------|
| Size reduction           | 1.656±0.010          | 2.680±0.011         | 61.47±0.08    | 13.15±0.02       | 25.38±0.10 | 364       | 322       | 88.5      |
| Without pretreatment     | 1.011±0.010          | 1.347±0.006         | 24.21±0.18    | 37.83±0.29       | 37.96±0.11 | 680       | 608       | 90.1      |
| 3%(w/v) NaOH             | 0.494±0.005          | 0.422±0.007         | 35.72±0.38    | 22.07±0.36       | 42.21±0.02 | 274       | 250       | 91.2      |
| 5%(w/v) NaOH             | 0.492±0.008          | 0.284±0.006         | 32.41±0.87    | 19.31±0.79       | 48.28±0.08 | 263       | 237       | 90.1      |
| 7%(w/v) NaOH             | 0.494±0.005          | 0.468±0.007         | 58.90±0.69    | 25.56±0.70       | 15.54±0.01 | 251       | 231       | 92.0      |
| Bio-scrubber effluent    | 0.745±0.005          | 1.424±0.005         | 58.48±0.15    | 27.24±0.15       | 14.28±0.00 | 302       | 267       | 88.4      |
| AS                       | 0.845±0.005          | 0.612±0.005         | 55.44±0.46    | 22.73±0.51       | 21.83±0.05 | 341       | 305       | 89.4      |

In term of reducing sugar, physical pretreatment by size reduction gave the highest concentration of reducing sugar. Pretreatment with chemical and biological methods resulted in lower concentrations of reducing sugar. This is because during chemical and biological pretreatment process, some sugar molecules are soluble into the pretreating solutions. With size reduction, there is no use of solution to leach sugar molecules from EFB. Moreover, microorganisms consume some sugar molecules for cell growth [12]. As a result, the concentration of reducing sugar decreased when EFB was pretreated with bio-scrubber effluent and AS. In term of carbohydrate analysis, similar trend as reducing sugar was observed. For pretreatment with bio-scrubber effluent, it is surprisingly found that the concentration of carbohydrates in EFB after pretreatment increased. This is probably due to the presence of carbohydrate contaminated in bio-scrubber effluent before the pretreatment process.
As shown in Table 1, the original cellulose content of EFB was 24.21%. All pretreatment methods increased the cellulose content of EFB differently. The cellulose composition of EFB most increased with the physical pretreatment (size reduction) to 61.47%. The pretreatments of EFB with 7% NaOH and bio-scrubber effluents gave similar cellulose contents (58.90% and 58.48%, respectively.) The pretreatment with AS gave slightly lower cellulose content (55.44%) than those with 7% NaOH and bio-scrubber effluent. It is important to point out that low concentrations (3% and 5%) of NaOH could slightly increase the cellulose content, unlike the pretreatment with high concentration (7%) of NaOH. In term of lignin content, the same trends were obtained. Low concentrations (3% and 5%) of NaOH solution could not decrease lignin content but instead increased the lignin content from 37.96% to 42.21% and 48.28%, respectively. The lignin content decreased only when high concentration (7%) of NaOH solution was used. Other pretreatment methods (physical and biological) were found to decrease the lignin contents of EFB as shown in Table 1. Therefore, it can be concluded that chemical pretreatment with high concentration of NaOH was the most effective method to decrease lignin component of original EFB. For hemicellulose content, all pretreatment methods decreased the hemicellulose contents significantly. The hemicellulose contents of EFB after size reduction was the lowest (13.15%).

The original EFB without pretreatment had TS and VS contents of 680 and 608 g/kg as shown in Table 1. The VS/TS ratio was 89.4%. Only chemical treatment increased the VS/TS ratio.

3.2. Effect of EFB pretreatment on Biochemical Methane Potential (BMP)

All pretreated and non-pretreated EFB samples were subjected to anaerobic digestion. As shown in Figure 1, the yield of methane was calculated from the composition of methane in biogas produced. All pretreatment methods of EFB could increase the yield of methane compared to untreated EFB. The physical method (size reduction) gave the highest yield of methane (429.9 ml/g.VS). In descending order, the yields of methane were 345.5, 326.4, 324.1, 314.6 and 297.3 ml/g.VS for pretreatments with 7% NaOH, bio-scrubber effluent, 3% NaOH, 5% NaOH and AS, respectively. However, the concentrations of methane in biogas products were indifferent significantly with all pretreatment methods. The concentrations were between 50.9-52.9% as shown in Figure 1.

![Figure 1. Methane yield of EFB pretreatment](image)

The increased yields of methane produced from pretreated EFB are due to the change in cellulose and lignin compositions of EFB after the pretreatment process. Size reduction increases the surface area, destroys the outer cell wall and removes some lignin structures resulting in more accessibility of microorganisms to digest cellulose and hemicellulose [12]. Moreover, the availability of small sugar molecules (see Table 1) which are readily digestible by microorganisms are promoted. Similarly, treatment with NaOH could dissolve some lignin components from EFB leaving the remaining
structures (cellulose and hemicellulose) to be digested easily. For biological treatment, hemicellulose could be decomposed by a microorganism (i.e. α-glucuronidase, α-arabinofuranosidase, acetoxylan) and enzymes (i.e. Actinomycetes) [13]. Typically, the digestibility of cellulose and hemicelluloses depends on pH, temperature, contact time, porosity, crystallinity degree, and the presence of hydrolyzing enzyme [14,15]. Acids and bases dissolved in bio-scrubber effluent might also influence the removal of hemicellulose and lignin from EFB.

3.3. Kinetic Models

The curve-fitting of the corrected Gompertz model to the experimental data for describing the accumulative biogas evolution (ABE) is presented in Figure 2. The model parameters were evaluated and summarized in Table 2. For all kinds of different pretreatment methods, it was found that Gompertz model could fit all data sets reasonably ($R^2 > 0.95$).

![Figure 2. Accumulative biogas production for corrected Gompertz model](image)

Table 2. Parameters of the corrected Gompertz model

| Pretreatment       | $P_e$ (ml) | Without | 3% w/v NaOH | 5% w/v NaOH | 7% w/v NaOH | Bio-scrubber effluent | AS |
|--------------------|------------|---------|-------------|-------------|-------------|-----------------------|----|
| Size reduction     | 2,991      | 2,933   | 1,843       | 1,779       | 1,822       | 1,990                 | 2,021 |
| Physical pretreatment | 0.083     | 0.080   | 0.068       | 0.071       | 0.070       | 0.068                 | 0.068 |
| 3% (w/v) NaOH      | 0.225      | 0.202   | 0.179       | 0.185       | 0.183       | 0.172                 | 0.175 |
| 5% (w/v) NaOH      | 94.03      | 90.43   | 50.16       | 48.89       | 50.84       | 52.82                 | 54.81 |
| 7% (w/v) NaOH      | 215.2      | 266.0   | 157.5       | 150.4       | 155.4       | 183.4                 | 183.2 |
| Bio-scrubber effluent | 6.199     | 4.651   | 6.311       | 5.907       | 6.170       | 5.407                 | 5.708 |
| AS                 | 0.985      | 0.982   | 0.995       | 0.997       | 0.990       | 0.987                 | 0.985 |

When looking closely, all curves had similar discrepancies. The corrected Gompertz model equation was under-fitted in the initial period (0-5 days) while over-fitted in the second period (5-20 days). This suggests that EFB, as a substrate for AD, is composed of complex nutrients that cannot be treated as one entity. The corrected Gompertz model is typically based on one substrate as the limiting substrate. It is customary to treat this type of ABE curves as composed of two main fractions. According to Table 2, the biogas production rate ($R_{m}$) was the highest with physical pretreatment (size reduction).

4. Conclusion

The most efficient pretreatment method of EFB was physical pretreatment (size reduction) which increased the methane yield from 226.0 to 429.9 ml/g.VS (>90% increase). This is due to the increases
in surface area, cellulose content and, most importantly, the concentration of reducing sugar which is readily digested by microorganisms. The pretreatment of EFB with NaOH had comparable effect as biological pretreatment but required chemicals and extra cost. Therefore, the effluent from bio-scrubber and AS could be used to pretreat EFB economically; the biogas yields increased up to 30% compared to untreated EFB. This is a promising method to reduce the wastes in palm oil mills as well as increasing the yield of biogas. The corrected Gompertz model could reasonably fit the experimental data of all pretreatment methods ($R^2 > 0.95$).

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References
[1] The Office of Agricultural Economics, OAE. 2018. Data of agricultural economic crop. In: Palm oil. Agricultural statistics of Thailand 2018. Ministry for Agricultural and Cooperatives.
[2] Yunus R, Salleh S F, Abdullah N and Biak D R A 2010 Effect of ultrasonic pretreatment on low temperature acid hydrolysis of oil palm empty fruit bunch J. Bioresour Technol. 101, 9792-9796.
[3] Han M, Kim Y, Kim S W and Choi G-W 2011 High efficiency bioethanol production from OPEFB using pilot pretreatment reactor J. Chemical Technology Bioethanol 86, 1527-1534.
[4] Kim S, Park J M, Seo J W and Kim C H 2012 Sequential acid-/alkali pretreatment of oil palm empty fruit bunch fibres J. Bioresour Technology 109, 229-233
[5] Taherzadeh M J, Karimi K 2008 Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review J. Mol Sci 9, 1621-1651.
[6] O-Thong S, Boe K, and Angelidaki I 2012 Thermophilic anaerobic co-digestion of oil palm empty fruit bunches with palm oil mill effluent for efficient biogas production J. Applied Energy 93, 648–654.
[7] Nieves D C, Karimi K and Horváth I S 2011 Improvement of biogas production from oil palm empty fruit bunches (OPEFB) J. Industrial Crops and Products 34, 1097–1101.
[8] APHA, 2012 Standard methods for the examination of water and waste water 22nd edn. American Public Health Association, Washington, DC.
[9] AOAC, 1997 Official method analysis, The Association of Official Analytical Chemist, 16th ed., AOAC, International, 28-90.
[10] Ayeni A O, Adeeyo O, Oresegun O and Oladimeji T 2015 Compositional analysis of lignocellulosic materials: Evaluation of an economically viable method suitable for woody and non-woody biomass J. Engineering Research 4, 14-19.
[11] Siripatana C, Jijai S and Kongjan P 2016 Proc.Int. Conf. Analysis and extension of Gompertz-type and Monod-type equations for estimation of design parameters from batch anaerobic digestion experiments 1775, 1-8.
[12] Zheng Y, Zhao J. Xu F and Li Y 2014 Proc.Int. Conf. on Energy and Combustion Science Pretreatment of lignocellulosic biomass for enhanced biogas production, 1-19.
[13] Jorgensen H, Kristensen J B and Felby C 2007 Enzymatic conversion of lignocellulose into fermentable sugars: Challenges and opportunities J. Biofuels Bioprod. Biorefin 1, 119-134.
[14] McIntosh S and Vancov T 2010 Enhanced enzyme saccharification of Sorghum bicolor straw using dilute alkali pretreatment. Bioresour J. Technol 101, 6718–6727.
[15] Liu Z, Fatehi P, Sadeghi S and Ni Y 2011 Application of hemicelluloses precipitated via ethanol treatment of pre-hydrolysis liquor in high-yield pulp J. Bioresour. Technol 102, 9613-9618.