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Kinetic Study of Alkaline Treatment in the Production of Bio-gas from Cocoa Pod Husks Using a Batch Reactor

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Abstract: Cocoa pod husk (CPH) is one of the potential plantation wastes used for biogas production. However, the presence of lignin inhibits the production process. Therefore, pretreatment is required to reduce the lignin content. This study investigates the effect of several pretreatment methods on lignin reduction and biogas production enhancement. The study also investigates the kinetic models for biogas production from treated and untreated CPH. The pretreatment exploitation NaOH (N), NaOH with the addition of H_2O_2 at the same time (NHS) and consecutively (NHC) were administered to cut back lignin content in CPH and enhance methane series yield. The N, NHS, and NHC pretreatments obtained the maximum delignification of 78.10%, 91.42%, and 88.68%. Biogas production from NHS pretreated with CPH led to a better methane yield (0.0389 m3CH4 / kgVS) than the various pretreatments corresponding to 175.59% for CPH without pretreatment and productivity is 0.0009 m3CH4 / kgVS.day. The biogas production kinetic model parameters have been evaluated by fitting experimental data for the treated and untreated cocoa waste. The kinetic models investigated are the one-step first-order kinetic model, two-step first-order kinetic models, Gompertz model, and Transfer Function model. Based on Root Mean Square Error (RMSE) value, the one-step first-order model is more accurate than the two-step first-order model. When compared with other models, the Gompertz model is the best version.

Keywords: alkaline treatment, kinetic model, biogas, cocoa pod husk.

间歇反应器碱处理可可豆壳生产沼气的动力学研究

摘要：可可豆荚壳是用于沼气生产的潜在种植园废弃物之一。然而，木质素的存在抑制了生产过程。因此，需要进行预处理以降低木质素的含量。本研究调查了几种预处理方法对减少木质素和提高沼气产量的影响。该研究还研究了从处理过和未经处理的可可豆壳产生沼气的动力学模型。采用氢氧化钠、氢氧化钠同时添加和连续预处理，降低可可豆壳中木质素含量，提高甲烷系列产率。两种添加物的氢氧化钠预处理获得了78.10%、91.42%和88.68%的最大脱木素。用可可豆壳预处理的氢氧化钠同时加入过氧化氢产生的沼气产生的甲烷产量（0.0389质量3甲烷 / 公斤力）比没有预处理的可可豆壳对应于175.59%的各种预处理更好，生产率为0.0009质量3甲烷 / 公斤力. 日。通过拟合处理和未处理可可废料的实验数据，评估了沼气生产动力学模型参数。研究的动力学模型是一步一级动力学模型、两步一级动力学模型、冈佩尔茨模型和传递函数模型。基于均方根误差值，一步一阶模型比两步一阶模型更准确。与其他模型相比，冈佩尔茨模型是最好的版本。

关键词：碱处理, 动力学模型, 沼气, 可可豆壳

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1. Introduction

Energy production from non-renewable sources has become a global problem in recent years, including Indonesia. According to available data, world energy sources comprised coal totaling 157.86 million tonnes (0.6% decrease from the previous year), natural gas total-ling 3.929 trillion m3 (2.0% increase from the previous year), and crude oil totaling 98.272 million barrels per day (an increase of 0.9% from the previous year). These non-renewable sources are predicted to become exhausted in 2169, 2068, and 2066, respectively [1]. For Indonesia, consumption of these energy sources amounts to 115 million tonnes of coal, 7.5 million tonnes of natural gas, and 283 million barrels of oil. Given this phenomenon of high global energy demand, renewable energy sources such as biogas are needed to substitute existing fossil fuels. Biogas is produced by bacterial degradation of biomass under anaerobic conditions. The main component of biogas is methane (CH4), along with several other substances such as carbon dioxide (CO2), water (H2O), and hydrogen sulfide (H2S) [2].

Biogas can be produced from various biomass, some from the agricultural and plantation sectors. Indonesia is one of the world’s largest cocoa producers, with 280 thousand tons of cocoa fruit being produced in 2018 [3]. In cocoa production, 67–76% of the crop harvested comprises a cocoa shell (CPH), and this waste product is often used in animal and poultry feed. It contains, among other substances, cellulose (35%), hemicellulose (11%), lignin (14.6%), pectin (6.1%), crude fiber (22.6%), raw protein (5.9%), and ash (9.1%) [4]. The composition of the compounds found in CPH can be seen in Table 1.

Although the high amounts of hemicellulose and cellulose found in CPH make it suitable for use as a substrate for biogas production, the presence of lignin can inhibit biogas formation. Lignin acts as an adhesive because of the cross-links between cellulose and hemicellulose, which form the rigid three-dimensional structure of the cell wall. Because of this, lignin has to be removed through a pretreatment process so that optimal fermentation can occur [5]. The presence of pectin also affects biogas formation because its matrix structure envelops cellulose and hemicellulose and blocks their exposure to enzymes, making the material more difficult to degrade. After pretreatment, pectin can be removed from the lignin matrix to not interfere with fermentation [6].

Previous studies have used pretreatments to assist the biogas formation process [7]. The most commonly used pretreatments are NaOH, H2SO4, and H2O2, the latter also helping the delignification process in CPH. Previous research has studied the kinetics of biogas formation using batch digesters and the Gompertz kinetic model [8].

The present study aims to evaluate kinetic models to obtain the reaction rate constant (k) of biogas formation from CPH using pretreatment with NaOH (N), NaOH with the addition of H2O2 simultaneously (NHS), and successively (NHC), and for CPH without pretreatment (untreated). Kinetic calculations are useful for determining which pretreatments are most favorable for biogas formation and design parameters for expanding the digestion process from laboratory to pilot plant scale.

Table 1. Composition in CPH [9]

Component	Value (%)
Moisture	80.2
Ash	9.1
sProtein	5.9
Crude fiber	22.6
NDF	61.0
ADF	50.0
Nitrogen-free	62.2
Crude fat (ether extract)	1.2
Cellulose	35.0
Hemicellulose	11.0
Lignin	14.6
Pectin	6.1
Ca	0.32
K	3.18
P	0.15
Mg mg/kg	0.22
Na	3.1
Zn	40.4
Fe	90.1
Cu	7.2
Mn	33.6

2. Research Method

2.1 Raw Material Preparation

Data obtained from experimental results in previous research [7] (as presented in Fig. 3) were used in this study as the kinetic parameter data to be searched for initial substrate concentration prior to pretreatment for each variable for the N, NHS, and NHC treatments and the untreated substrate over 30 days.

In addition, data in the form of maximum biogas production rate (Rb) in mL/d, maximum biogas (B) produced in mL, and lag phase time (λ) in days are presented in Table 2. The final percentages of methane for the NHS, NHC, N and untreated variables were 50.12%, 43.55%, 31.30%, and 29.11%, respectively [7].

Table 2. Experimental data and results from [7]

Sample	B (mL)	Rb (mL/day)	λ (day)	Biogas yield (m^3 CH_4 / kg $VS_{removal}$)	S_0 (mg/L)
Untreated	322.74	20.086	6.08	0.0172	4288,9
N pret.	533.20	21.609	1.41	0.0309	4561.4
NHS pret.	527.44	24.525	1.60	0.0389	3173.3
NHC pret.	451.16	21.548	2.14	0.0265	3352.1

2.2. Kinetic Study

The kinetic study of this research used several models: Semitheoretical model (One-step reaction with first-order kinetics, and Two-step reaction with first-order kinetics) and empirical kinetic model (the modified Gompertz and transfer function model).

2.2.1. One-step Reaction Study with First-order Kinetics

The kinetics produced in this model is a kinetic rate constant (k) derived from a one-step reaction with first-order kinetics. The model can show that the rate of reaction is equal to the existing substrate, as indicated by Equations 1 and 2:

$$\frac{dS}{dt} = k\,S \qquad (1)$$

$$S = S_0\,e^{-kt} \qquad (2)$$

where notation S is the concentration of substrates at the time (t), S_0 is equal to the concentration of initial substrates, and notation k is equal to kinetics constant. For indicating substrate degradation, a reaction product in the form of methane (M) is formed and can be calculated by Equation 3:

$$M = S_0\,(1 - e^{-kt}) \qquad (3)$$

According to Angelidaki et al. [10], Equation 3 can be correlated using the methane concentration produced by the anaerobic digestion process through Equations 4 and 5:

$$M = M_e\,(1 - e^{-kt}) \qquad (4)$$

$$ln(\frac{M_e - M}{M_e}) = -kt \qquad (5)$$

where M is the methane produced, Me is the maximum methane production, and k is the hydrolysis constant. Research conducted by [11, 12] shows that there is no significant difference if Equation 5 uses the lag phase time (tlag) compared to the modified Gompertz model. However, the first-order kinetics equation has a longer tlag. Methane produced at maximum point (Me) in value 0.30 to 0.33 m3/kg SV, and we can use Equations 6 and 7, as follows:

$$M = M_e\,(1 - e^{-k(t - t_{lag})}) \qquad (6)$$

$$ln(\frac{M_e - M}{M_e}) = -k(t - t_{lag}) \qquad (7)$$

From Equation 5 and tlag, as in Equation 7, the gradient that can be created showing the plot on the y axis ($ln(\frac{M_e - M}{M_e})$) and the x-axis (t hydrolysis reaction) can be obtained. The parameters generated (k) are obtained through the estimates fitting the results of the experiments using the solver functions of MS Excel ToolPak

2.2.2. Two-step Reaction Study with First-order Kinetics

In addition to investigating one-step reaction kinetics with first-order kinetics, this research also uses two-step reaction kinetics with first-order kinetics. Methanogenic modeling, considered more suitable than the previous modeling, will form volatile fatty acids (VFAs) in the reaction obtained from the substrate, which will then be converted to methane (M). Based on mass equilibrium, the reaction forming VFA is obtained from the initial substrate converted first into VFA. VFA elimination reactions occur depending on the VFA concentrations formed. Denoting k2 as the kinetic constant of elimination of VFA, the formation of M from VFA is shown in Equations 8 and 9, as follows:

$$\frac{dS_{VFA}}{dt} = k_1\,S_0\,e^{-kt} - k_2\,S_{VFA} \qquad (8)$$

$$S_{VFA} = k_1\,S_0\,\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \qquad (9)$$

Equation 9 can be further derived to find the methane accumulation, which is formed as in Equations 10 and 11:

$$\frac{dM}{dt} = k_2\,S_{VFA} \qquad (10)$$

$$\mathrm{M} = S_0\left(1 - \frac{\mathrm{k}_1\,e^{-\mathrm{k}_2 t} - \mathrm{k}_2\,e^{-\mathrm{k}_1 t}}{\mathrm{k}_1 - \mathrm{k}_2}\right) \qquad (11)$$

where M is the methane formed in time (t), S0 is the number of initial substrates, k1 is the acetogenesis kinetic constant of VFA formation, and k2 is the kinetic constant of M formation of VFA. The resulting equation is then searched for both k1 and k2 through estimation utilizing experimental results carried out in previous studies using the solver optimization of the MS Excel ToolPak function.

2.2.3. Modified Gompertz model

Modified Gompertz model for the cumulative biogas generation is written in Equation 12.

$$\mathrm{Bt{=}B\ exp}\left(\text{- exp}\left[\frac{\mathrm{Rb} \times \mathrm{e}}{\mathrm{B}}(\lambda\text{-t}){+}1\right]\right) \qquad (12)$$

This model was created because modeling using the Monod equation was unsatisfactory. After all, it does not properly describe the variation in cell concentration when the substrate is consumed or during the stationary phase. Bt represents the cumulative biogas produced (mL), B is the maximum biogas production (mL), Rb means biogas production rate at maximum point (mL/d), λ means the lag time (time for bacteria to adapt) (d), t is incubation time (d). All parameters (B, Rb, and λ) were estimated by fitting the experimental results into the models via the solver function of the MS Excel ToolPak.

2.2.3. Transfer Function Model

The function transfer model was also used to compare modeling using one-step and two-step reactions. This model is similar to the first-order kinetic model, but the kinetic constant is converted to compare the maximum biogas yield and the methane production rate. Several studies [13-15] use this model as a reference to determine the amount of methane produced:

$$M = M_e\left(1 - e^{-k(t-tlag)}\right) \qquad (13)$$

$$= M_e\left(1 - e^{-\frac{vmaxM}{Me}(t-tlag)}\right) \qquad (14)$$

All parameters (vmaxM, Me, and tlag) were estimated by fitting the experimental results into the models via the solver function of the MS Excel ToolPak. The accuracy of kinetic models was compared using RMSE and Coefficient of determination (R^2 value). As seen in Fig. 1, the experimental flowchart describes clearly the experiment.

3. Results and Discussions

3.1. One-step Reaction Kinetic Study with First-order Kinetics

The kinetics of the anaerobic digestion reaction of the four treatments (NHS, NHC, N, and untreated) were obtained through linear regression from the graphs obtained from Equations 3 and 5. The graph results obtained are presented in Fig. 1 to 4.

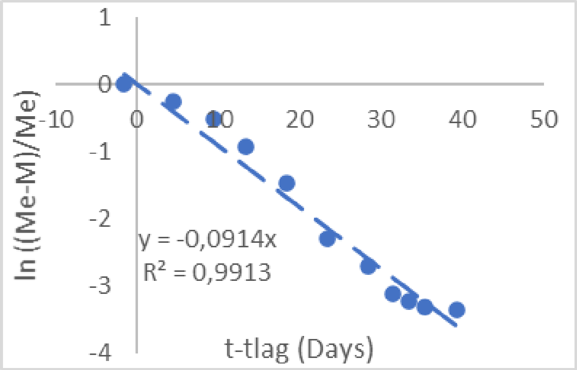

Fig 1. ln ((M_e-M)/M_e) vs. time (days) for treatment NHS.

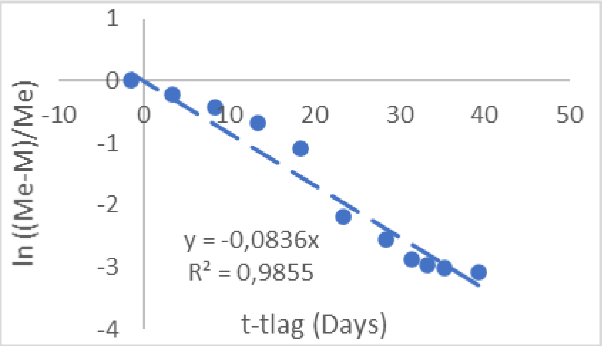

Fig 2. ln ((M_e-M)/M_e) vs. time (days) for treatment N.

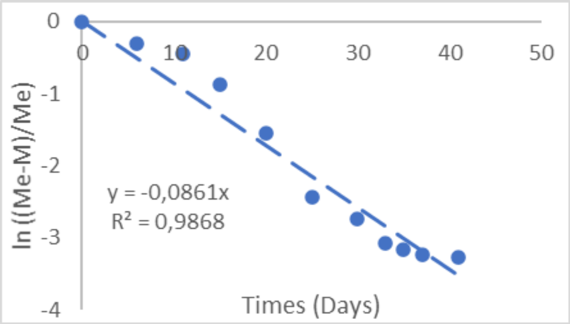

Fig 3. ln ((M_e-M)/M_e) vs. time (days) for treatment NHC

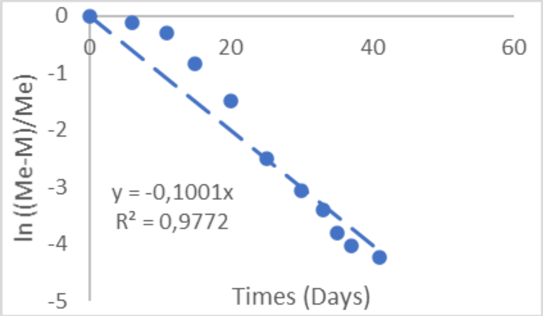

Fig 4. ln ((M_e-M)/M_e) vs. time (days) for untreated media.

The modeling approach used to find the reaction kinetics in treatments using NHS and N applies Equation 7. Meanwhile, the treatment using NHC and the untreated media uses Equation 3. That is because the maximum methane (M*e*) generated is between 0.30 and 0.33 m3/kg SV, as evidenced by the termination data coefficient (R^2) being greater than using Equation 3, meaning that the results obtained are more accurate than using Equation 3. Based on Fig. 1 to 4, the acetogenesis kinetics constants obtained (k_1) from NHS, NHC, N treatments, and untreated medium were 0.0914, 0.0861, 0.0831, and 0.1001 day^{-1}, respectively.

Based on the results of the previous research, which were used as the relevant data in this study, it can be concluded that treatment using NHS is the fastest reaction and has the highest yield (Table 1). The NHS treatment process is a delignification process that increases the efficiency of the alkaline treatment of lignin and enzymatic digestion [16]. The addition of H_2O_2, which is highly oxidative, helps the breakdown of lignin by attacking the lignin matrix chain so that the anaerobic digestion process can proceed more quickly.

3.2. Two-step Reaction Kinetic Study with First-order Kinetics

Other studies have shown that anaerobic digestion is a complex series of processes consisting of two major steps: the formation of VFAs from substrates processed by bacteria and the formation of methane from weak organic acids (VFAs) [17]. This study uses Equation 9 to find the kinetic constants of acetogenesis (k_1) and methanogenesis (k_2) with the help of solver optimization provided by MS Excel ToolPak. The k_1 and k_2 of NHS, N, NHC, and untreated substrate are described in Table 3.

Table 3. Kinetic constants

Sample	k (day^{-1}) (one-step)	k$_1$ (day^{-1}) (two-step)	k$_2$ (day^{-1}) (two-step)
Untreated	0.1001	12,758.20299	0.0006408
N pretreatment	0.0836	0.99248	0.001036
NHS pretreatment	0.0914	0.00212	9,903,653.205
NHC pretreatment	0.0861	52,895,454.54	0.00174
Untreated	0.1001	12,758.20299	0.0006408

The process of biogas formation occurs through a series of complex processes. The bacterial fermentation process occurs under anaerobic conditions. Anaerobic fermentation consists of four major processes, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis [18]. The hydrolysis process converts complex polymer compounds (carbohydrates, proteins, and lipids) into monomers and oligomers (glucose, amino acids, and peptides). In acidogenesis, these components are converted into low-chain organic acids (VFAs). Then VFAs are converted into acetic acid, H_2, and CO_2 and then finally converted into biogas (methane) through the methanogenesis process. In the hydrolysis process, phyla often encountered are Chloroflexi, Thermotogae, Firmicutes, Bacteroidetes, Proteobacteria, and Spirochaetes [18]. The role of hydrolytic bacteria is in assisting the hydrolysis process to make cellulosomes. This multienzyme process produces various hydrolase enzymes, such as glucanases, hemicellulases, chitinases, and lihanases. Therefore, hydrolytic bacteria can decompose complex organic compounds [19].

In the acidogenesis process, the decomposition results of complex compounds are used to form weak organic acids (VFA) [18]. Several bacterial phyla are found in this process, including Firmicutes, Bacteroidetes, Proteobacteria, and Actinobacteria. Some of the species that have been isolated include *Clostridium* (Firmicutes), *Peptococcus* (Firmicutes), *Bifidobacterium* (Actinobacteria), *Desulfovibrio* (Proteobacteria), *Corynebacterium* (Actinobacteria), *Bacillus* (Firmicutes), *Pseudomonas* (Proteobacteria), and *Desulfobacter* (Proteobacteria) [20, 21]. The fermentation process using a substrate from among the hydrolysis products produces a wide range of weak organic acids (VFA) such as formic acid, acetic acid, propionate acid, butyric acid, pentanoate acid as well as alcohol, H_2, and CO_2 [22].

Furthermore, weak organic acids (VFA) are processed into acetic acid and H_2 and CO_2 gases through the acetogenesis process. This process requires the help of bacterial acetogenesis, better known as syntrophic acetate oxidization or SAO. The acetogenesis process determines the success of the anaerobic fermentation process because about 70% of methane is produced from acetate reduction. The phyla of bacteria often encountered in acetogenesis are Pseudothermotoga letting, Thermacetogenium phaeum, Syntrophaceticus schinkii, and Spirochaetes [23-25]. The final process is the formation of biogas (methane) through the methanogenesis process with the help of methanogenic bacteria. The most commonly encountered methanogens have been recorded as belonging to up to 65 species identified and grouped into five groups, namely Methanobacteriales, Methanococcales, Methanomicrobiales, Methanosarcinales, and Methanopyrales [26, 27]. Based on the substrate produced by these methanogenic bacteria, they can be grouped into three sub-divisions: methylotrophic methanogens that produce metals and other single-chain carbons; hydrogeologic methanogens which produce CO_2 and H_2; and aceticlastic methanogens which produce acetate [18]. The resulting model, especially for two-step first-order kinetics, assumes two major reactions, namely acetogenesis and methanogenesis. These two reactions are considered to be the main processes, as indicated by the quantity of the substrate produced from a series of anaerobic fermentation processes.

3.3. Kinetic Study Using Other Models

The function transfer model was also used to compare modeling using one-step and two-step reactions. This model is similar to the first-order kinetic model, but the kinetic constant is converted to compare the maximum biogas yield and the methane production rate. Several studies [13-15] use this model as a reference to determine the amount of methane produced:

$$M = M_e \left(1 - e^{-k(t-tlag)}\right) \tag{15}$$

$$M = M_e \left(1 - e^{-\frac{vmaxM}{Me}(t-tlag)}\right) \tag{16}$$

Another model used as a comparison is the Gompertz model. It was created because modeling using the Monod equation was unsatisfactory. After all, it does not properly describe the variation in cell concentration when the substrate is consumed or during the stationary phase. As a result, research conducted by Winsor [28] uses the equation proposed by Gompertz [8] in his research on human demographics, as shown in Equations 17 and 18, in which a and c are constants

$$\frac{dX}{dt} = c\, ln(\frac{a}{X})\, X \tag{17}$$

$$\mu = c\, ln(\frac{a}{X}) \tag{18}$$

In Equation 17, the Gompertz equation shows cell growth without limitation. If there is a maximum limit, the derivation of Equation 17 will not work at a particular point and is then solved to obtain the cell concentration function, as in Equations 19 and 20:

$$\frac{ln(\frac{a}{X0})}{e^{ct}} = ln(\frac{a}{X}) \tag{19}$$

$$X = a\, e^{[-e^{-ct+b}]} \tag{20}$$

Substituting in the equation $b = c\, tlag + 1$ dan $vmax = \frac{a\, c}{e}$, the Gompertz modification a is expressed as the concentration of the maximum cell [29]:

$$X = a\, e^{(-e^{\frac{vmax\, e}{Me}(tlag-t)+1})} \tag{21}$$

To find an equation to obtain the biogas produced, Equation 18 becomes Equation 19:

$$M = Y_{P/X}\ a\ e^{\left(-e^{\frac{vmax\ e}{Me}(tlag-t)+1}\right)} \qquad (22)$$

Research by Lay [30] modified the Gompertz equation by expressing M_e = YP/X so that it becomes Equation 20:

$$M = M_e\ e^{(-e^{\frac{vmax\ e}{Me}(tlag-t)+1})} \qquad (23)$$

Most researchers use the root mean square error (RMSE) method to compare the models used as in Equation 21. M_{model} is the methane result predicted by existing modeling, and M_{obs} is the methane produced and observed experimentally.

$$RMSE = \sqrt{\frac{\sum(Mmodel-Mobs)^2}{n}} \qquad (24)$$

A comparison of the one-step and two-step models is presented in Table 4. It can be seen that the error results generated by one-step modeling for all processes except without treatment are smaller than those generated by two-step modeling. So it can be concluded that the model with the higher accuracy is the one-step model. From the RMSE value, it turns out that the one-step order model is more accurate than the one-two-step order model. For the two-step model, there is a very big difference from the value of the reaction rate constant for step one and step two, meaning that there is a controlling step. That is why the one-step model is more accurate than the two-step model. However, the most accurate modeling approach uses the modified Gompertz model, which shows more accurate cell characteristics because reviewing cell characteristics for the substrate consumed also observes cell growth in the stationary phase. The Monod equation, which is often used, assumes the performance of cells for substrate degradation at their maximum growth point [28].

It shows that N and NHs pretreatment can properly increase the rate of bacteria in degrading organic materials. However, the quality of NHS pretreatment is better because it has a higher methane gas content than N pretreatment. In contrast, bacterial acclimatization occurs the longest on the untreated substrate, which is almost 4 times longer than the N and NHS pretreatment. That shows the influence of lignin as a bacterial inhibitor to degrade organic materials (cellulose and hemicellulose) in CPH. The experiment shows that the presence of H_2O_2 on pretreatment can increase methane yield because more lignin can be degraded. The addition of the pretreatment reagent directly shows higher biogas and methane yields because the continuous addition can disrupt biomethane formation.

Table 4. Comparison in the model in RMSE

Sample	**RMSE (one-step)**	**RMSE (two-step)**	**RMSE (Transfer function)**	**RMSE (Gompertz)**
Untreated	28.9005	11.649	52.209	0.884
N pretreatment	1.413	12.968	84.062	2.5201
NHS pretreatment	19.703	32.825	124.35	4.314
NHC pretreatment	30.677	25.42	95.872	4.3528
Untreated	28.9005	11.649	52.209	0.884

Continuation of Table 4

4. Conclusion

Pretreatment is required to increase biogas productivity. The treatments performed in this study were NHS, N, NHC, and untreated. Modelling is performed using one-step first-order kinetics with constants k of 0.0914; 0.0831; 0.0861; and 0.1001(day-1), respectively. Two-step first-order kinetics produce constants k1 of 0.00212; 0.99248; 52,895,454.54 and 12,758.202 (day-1) and k2 9,903,653.205; 0.001036, 0.00174 and 0,0006408 (day-1). Based on the experimental results, treatment NHS is the best for resulting biogas yield, with a maximum of 0.0389 m3 CH4/kg VS removal and a high rate of kinetic of 0.0914 (day-1). In comparing the first-order and second-order models, the first-order model is the best because its RMSE value is smaller when compared to the second order. When compared with other models, the Gompertz model is the best version. Forming biogas consists of 2 main processes, the formation of product intermediates (VFA) and the formation of biogas (methane). In the acidogenesis process that produces VFA, bacteria that are often found include Clostridium (Firmicutes), Peptococcus (Firmicutes), Bifidobacterium (Actinobacteria), Desulfovibrio (Proteobacteria), Corynebacterium (Actinobacteria), Bacillus (Firmicutes), and Pseudomonas (Firmicutes). Desulfobacter (Proteobacteria). VFA is converted into acetic acid in forming biogas, which eventually becomes methane. Bacteria that convert VFA into acetic acid include Pseudothermotoga lettingae, Thermacetogenium phaeum, Syntrophaceticus schinkii, and Spirochaetes. Bacteria that convert acetate to methane include Methanobacteriales, Methanococcales, Methanomicrobiales, Methanosarcinales, and Methanopyrales.

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