Performance of biogas production from coffee pulp waste using semi-continuous anaerobic reactor

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Abstract. The abundant coffee pulp waste can be used as a potential biogas feedstock due to its high cellulose and hemicellulose content. However, it contains lignin that difficult to be digested and caffeine and tannin that cause severe effects on microbial activity inside the digester. Therefore, alkaline hydrogen peroxide (AHP) followed by rumen fluid pretreatment had been performed to remove those compounds and improve digestibility of the substrate. Moreover, the study obtained to find the reaction kinetics in biogas production from coffee pulp waste using a semi-continuous anaerobic reactor with HRT 20, 25, 30 and 35 days and a working volume of 1.5 L operated at 37 °C. In this study, the AHP pretreatment resulted in 75% of lignin removal, 57.76% of caffeine removal and a decrease in tannin until 0.54%. The highest methane yield obtained in this study was 0.24 L CH₄ g VS⁻¹. The kinetic constants (k) obtained were; k₁ (reaction’s kinetic constant): 0.2923 day⁻¹; k₂ (maximum rate of soluble organics production/ degradation): 720.1309 mg SCOD L⁻¹ day⁻¹; k₃ (saturation constant): 253.2091 mg SCOD L⁻¹ day⁻¹; k₄ (maximum rate of TVA consumption): 1,426.0831 mg TVA-COD L⁻¹ day⁻¹; and k₅ (saturation constant): 57,794.4025 mg TVA-COD L⁻¹ day⁻¹.

1. Introduction
Energy is people’s basic needs. The dependence of non-renewable energy like fossil fuel has caused an energy availability crisis. Thus, alternative renewable energy sources such biogas are highly needed. Biogas is an odorless and colorless gas that burns with clear blue flame which obtained from anaerobic decomposition. Microorganisms transforms organic materials under oxygen-free conditions into biogas, nutrients and additional cell matter, leaving salts and refractory organic matter. Raw biogas typically consists of CH₄ (60%), CO₂ (40%) and other trace compounds such as hydrogen sulfide [1].

Biogas can be produced from various sources, such as agro-industrial waste. One of which is coffee pulp waste (CPW) [2]. It is abundant where Indonesia is the fourth largest coffee producer country in the world with 620,000 tons production in 2019 [3]. About 30-50% of the total weight of coffee cherries is CPW [4].

CPW contains cellulose and hemicellulose that can be converted to biogas. But it also contains lignin, caffeine and tannin which have negative effects on the fermentation process. Lignin binds cellulose and hemicellulose, reducing their biodegradability. Caffeine and tannin can inhibit bacterial growth during the fermentation process [5]. It has been reported that 0.0025 g mL⁻¹ of caffeine was capable to inhibits the growth of many bacterial species [6]. Tannin can bind protein and other polysaccharide compounds which are needed for microbial growth [7]. Therefore, the pretreatment process is required to eliminate...
or reduce inhibitor compounds so the fermentation process can be optimized and resulting in higher biogas production.

The pretreatment using alkaline hydrogen peroxide (AHP) has been applied in this study followed by rumen fluid pretreatment. Reference [8] have proved that alkaline pretreatment was capable of degrading lignin on sorghum stem as much as 29% and increasing methane production as much as 29%. Rumen fluid contains a complex microbial ecosystem (10^{10–11} cells mL^{-1} bacteria, 10^{3–5} cells mL^{-1} fungi and 10^{4–6} cells mL^{-1} protozoa) which is able to ferment lignocellulosic feed, including glycoside hydrolases and carbohydrate esterases, leading to efficiently produce volatile fatty acids (VFAs) as the precursor of biogas [9].

Biogas production industries tend to use a semi-continuous type reactor rather than a batch or continuous reactor. This will result in more optimal products. Compared to a batch reactor, the higher gas volume is produced by the semi-continuous reactor [10].

This study deals with the investigation of lignin and inhibitor content removal in coffee pulp waste using AHP and rumen fluid pretreatment. Also, to evaluate the influence of the pretreatment to the kinetic of biogas production using a semi-continuous reactor model.

2. Materials and Methods

2.1. Coffee pulp waste pretreatment

CPW was obtained from Malang, Indonesia and dried using solar radiation. The size of dried CPW was reduced to 100 mesh. Then, it was pretreated using 5% (v/v) H_{2}O_{2} solution at adjusted pH of 11.5 with the addition of NaOH. Pretreatment temperature was set at 80°C for 6 hours. The solid to liquid ratio was set for 1:9. Subsequently, the coffee pulp was filtered and washed with water until the pH was neutral, and then dried using an oven at 60°C. Finally, 60 grams of dried CPW were treated with 1.5 L of rumen fluid and incubated at 37 °C for 24 hours.

2.2. Semi-continuous anaerobic fermentation

Anaerobic fermentation was done in 2 L semi-continuous reactors which were made of PVC pipe and accompanied by a stirring motor. The working volume of the reactor was 1.5 L where there were 4 variables of hydraulic retention time (HRT), i.e. 20, 25, 30, and 35 days. Each of the HRT variables used an AHP-rumen fluid pretreated substrate. The resulted gas was collected in a gas holder.

2.3. Analytical method

The native CPW and CPW pretreated AHP was submitted to lignocellulosic analysis. Lignin and ash content were gravimetrically analyzed refers to [11]. Holocellulose, cellulose and hemicellulose were analyzed based on the methods of [12]. UV/Vis-spectrophotometer was used to determine caffeine content at a wavelength of 273 nm [13] and tannin at 725 nm [14]. The COD value was measured according to the procedure of [15]. Methane and carbon dioxide concentration in the resulted biogas were analyzed using gas chromatography (GC). VFA was analyzed refers to the method described by [5].

2.4. Kinetic study

To determine the reaction kinetics in biogas formation, the mathematical modeling which was performed based on the proposed methods by [16]. This model equation consists of some parameters, namely: k_{1} (reaction kinetics constant), k_{2} (maximum production/degradation rate of soluble organic materials), k_{3} (saturation constant), k_{4} (maximum production/degradation rate of Total Volatile Acid (TVA)), and k_{5} (saturation constant). Three equations were solved mathematically by the fourth-order Runge-Kutta method. k_{1} – k_{5} parameters were determined to obtain the minimum sum of squared deviations between simulation and experimental data. Those parameters are presented in equations (1)-(3).
\[
\frac{dS_{VSS}}{dt} = k_1 S_{VSS} \\
\frac{dS_{VDS}}{dt} = \frac{k_1 S_{VSS} - k_2 S_{VDS}}{k_3 + S_{VDS}} \\
\frac{dS_{TVA}}{dt} = \frac{k_2 S_{VDS} - k_4 S_{TVA}}{k_3 + S_{VDS} - k_5 + S_{TVA}}
\]

3. Results and Discussion

3.1. Biogas feedstock

Cellulose and hemicellulose components in CPW have become main sources in biogas production while lignin, caffeine and tannin are inhibitors in biogas formation. Reference [17] have reported that the co-digestion of cellulose and hemicellulose has a synergistic effect on methane yield.

Lignin plays the role of cement for the cross-linking between cellulose and hemicellulose to form a rigid three-dimensional structure of the cell wall [18]. Theoretically, the usage of NaOH is capable to degrade lignin because it can break down ester bonds between lignin structure [21]. The addition of \( H_2O_2 \) will weaken the matrix inside lignin [19]. Pretreatment with AHP in this research had lignin removal, about 75.02%. In another study of [20], the pretreatment of CPW using AHP with a concentration of 7.5% (w/w of substrate) for 24 hours at 35°C was reported only reduce the lignin content by 49.49%. The cellulose content in this study increased by 77.36% which was higher than biological pretreatment which were able to increase a portion of cellulose by 34.89% [5] and by 14.6% using organosolv pretreatment [21].

In other hands, the content of caffeine and tannin could also be reduced through the AHP pretreatment. A native CPW had a caffeine level of 14.58 ppm (see Table 1), while after pretreatment, its level decreased until 6.16 ppm or decreased by 57.76%. Tannin concentration in native CPW was 2.16% and decreased until 0.54% after AHP pretreatment.

| Compounds      | Native CPW  | Pretreated CPW |
|----------------|-------------|---------------|
| Lignin         | 42.10%      | 10.51%        |
| Cellulose      | 38.52%      | 68.32%        |
| Hemicellulose  | 5.88%       | 7.00%         |
| Caffeine       | 14.58 ppm   | 6.16 ppm      |
| Tannin         | 2.16%       | 0.54%         |
| Others         | 11.34%      | 13.53%        |

Table 1. Chemical compounds in native and pretreated CPW using AHP

![Figure 1. Alteration of acetic acid (A) and chemical oxygen demand (B)](image)
3.2 Volatile fatty acid (VFA)
One of the functions of rumen fluid is to produce VFA. High VFA concentration can decrease the pH of the solution in the digester. The proportional VFA concentration can also increase biogas production if the pH condition is neutral [22]. Figure 1A shows the VFA concentration as acetic acid during fermentation process. Initial condition (VFA=0) was started 1 day before CPW and rumen fluid were put into the reactor (data are not shown). From Figure 1A, it can be seen that at the first 5 days were the most productive time in VFA production. In the first 10 days, hydrolysis and acidification probably happen simultaneously where the complex organic molecules which are hydrolyzed to monomers or soluble molecules and are instantly processed by acidogenic bacteria to produce VFA. VFA production tended to slow down after 11 days until reaching its maximum after 20-25 days.

3.3 Chemical oxygen demand (COD)
COD is the amount of required oxygen to oxidize waste materials in water via chemical reaction. COD also can easily quantify the amount of organics in water. From Figure 1B, it can be seen that COD was decreasing in value because the organic molecules have been degraded by bacteria. Although feeding was done every day, COD value kept decreasing, which indicating that degradation by bacteria has a bigger value than the biomass that enters via feeding. In the first 10 days, the COD value decreased rapidly. This is caused by the degradation of organic molecules to the simpler and soluble molecules which are then processed into acid (VFA). Then, during day 11 to 20, COD values tended to be constant. At this stage, the acetogenesis process has occurred where VFA other than acetate will be converted to acetate. The methanation process also has occurred and produced CH₄ from CO₂ and H₂. Final COD value on day 30 for HRT 20, 25, 30, and 35 consecutively was 294, 205, 504, and 156 ppm with COD removal of 89.01%, 91.48%, 81.15%, and 93.54%.

3.4. Biogas production and kinetic
Based on the result, variable with bigger HRT value could produce biogas in higher volume and methane concentration. The best variable was HRT 35 which resulted in biogas of 13.031 L with CH₄ dan CO₂ concentration of 53.31% and 27.29%, respectively. Substrate residence time inside the reactor will influence the methanation phase. If the substrate resides longer, the formation of methane gas will increase. HRT 35 was the optimal residence time that still was economical.

Table 2. Comparison of methane yield from different studies

| Substrate      | Reactor Type                | Yield         | Reference |
|----------------|-----------------------------|---------------|-----------|
| CPW + cow dung | Batch                       | 0.065 L CH₄ g VS⁻¹ | [23]      |
| CPW            | Continuous Stirred Tank Reactor | 0.234 L CH₄ g VS⁻¹ | [24]      |
| CPW            | Semi-continuous             | 0.24 L CH₄ g VS⁻¹ | This study|

Table 2 shows that the semi-continuous reactor has advantages where the resulting a higher biogas yield compared to batch and continuous reactor. In a semi-continuous reactor, the substrate resides in a reactor for a certain time (HRT) so the methanation process can occur optimally. In a continuous reactor, the substrate resides in a short time so the methanation process has not occurred optimally. While in a batch reactor, no new substrate is inserted so that the biogas production does not increase properly.

All kinetic parameters have been obtained as shown in Table 3. From the three models, the R² value is more than 0.9. This shows that the parameters obtained are suitable for use in modeling this biogas production. Model of hydrolysis shows that the greater the HRT value, the fewer volatile suspended solid (VSS) present. In this step, complex organic compounds are hydrolysed by enzymes from hydrolytic bacteria that will produce soluble monomers (amino acid, glucose, fatty acid, and glycerol). For acidification model, the longer HRT affected the less remained volatile dissolved solid (VDS) materials. Rapid reduction in VDS content is caused by high fermentative acidogenic bacteria concentration from rumen fluid, so the conversion of VDS to TVA become faster. Then, it can be seen
in methanation model that TVA content increased rapidly in HRT less than 10. Furthermore, TVA begins to decline slowly. The decline in TVA shows that biogas production is starting to occur.

**Table 3.** Value of kinetics study

| Parameter | Value       | Model equation | Step       | R²  |
|-----------|-------------|----------------|------------|-----|
| k₁        | 0.2923      | \(-\frac{dS_{VSS}}{dt} = 0.2923 S_{VSS}\) | Hydrolysis | 0.999 |
| k₂        | 720.1309    | \(\frac{dS_{VDS}}{dt} = 0.2923 S_{VSS} - \frac{720.1309 S_{VDS}}{253.2091 + S_{VDS}}\) | Acidification | 0.996 |
| k₃        | 253.2091    | \(\frac{dS_{TVA}}{dt} = \frac{720.1309 S_{VDS}}{253.2091 + S_{VDS}} - \frac{1,426.0831 S_{TVA}}{57,794.4025 + S_{TVA}}\) | Methanation | 0.922 |

![Graph](image.png)

**Figure 2.** Fitting of kinetic model (---) to experiment data (◊) for hydrolysis (A), acidification (B), and methanation (C).

**4. Conclusion**

In this research, NaOH-H₂O₂ pretreatment is capable to decrease lignin content and other inhibitors such as caffeine and tannin. Lignin, caffeine and tannin concentration decreased by 75%, 57.76%, and 0.54 %, respectively. The best result of biogas was obtained in the reactor with HRT of 35 days with a volume of 13.031 mL and a CH₄ concentration of 53.313%. Kinetic parameters were successfully investigated in semi-continuous reactor. This type of reactor has advantages in producing biogas compared to batch and continuous reactor.

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