The Effect of Acid Pre-Treatment using Acetic Acid and Nitric Acid in The Production of Biogas from Rice Husk during Solid State Anaerobic Digestion (SS-AD)

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Abstract. Pretreatment during biogas production aims to assist in degradation of lignin contained in the rice husk. In this study, pretreatment which is used are acid and biological pretreatment. Acid pretreatment was performed using acetic acid and nitric acid with a variety levels of 3% and 5%. While biological pretreatment as a control variable. Acid pretreatment was conducted by soaking the rice straw for 24 hours with acid variation. The study was conducted using Solid State Anaerobic Digestion (SS-AD) with 21% TS. Biogas production was measured using water displacement method every two days for 60 days at room temperature conditions. The results showed that acid pretreatment gave an effect on the production of biogas yield. The yield of the biogas produced by pretreatment of acetic acid of 5% and 3% was 43.28 and 45.86 ml/gr.TS. While the results without pretreatment biogas yield was 29.51 ml/gr.TS. The results yield biogas produced by pretreatment using nitric acid of 5% and 3% was 12.14 ml/gr.TS and 21.85 ml/gr.TS. Results biogas yield with acetic acid pretreatment was better than the biogas yield results with nitric acid pretreatment.

1 Introduction

According to Minister of Energy and Mineral Resources, the dependence on fossil fuels, particularly oil in fulfilling domestic consumption is still high at 96% (petroleum 48%, gas 18% and coal 30%) of the total consumption and to maximize the utilization of energy renewable not capable of running as planned. Indonesian government's efforts in dealing with the energy issue is with the issuing of Law No. 5/2006 on the use of new and renewable energy.

Indonesia is an agricultural country with a large agricultural sector. One of the major agricultural sector is rice. Agricultural waste is containing lignocellulosic biomass. Rice straw is composed of three types of main components, cellulose, hemicellulose, and lignin. Cellulose and hemicellulose can be hydrolyzed to monosaccharides or simple sugars and can be fermented to biogas [1]. However, one of the problems in the production of biogas from biomass lignin is resistance to biodegradation or hydrolysis [2]. A key success factor for biogas production is to increase the efficiency of hydrolysis of biomass with increasing accessibility enzyme through pretreatment method [3]. Pretreatment using organic acids have several desirable characteristics, hydrolysis effective, less degradation products, and produce more sugar [4].

Pretreatment is a method to reduce or eliminate impurities or undesirable compounds in the raw material to be made into a product. In the process of biogas production from rice straw using a pretreatment in the form of delignification [5]. Chemical pretreatment refers to the use of chemicals, such as acids, bases, and ionic liquids to change the physical and chemical characteristics of lignocellulosic biomass [6]. Delignification process chemically induced by mixing and soaking acidic or alkaline compounds in the raw material before the fermentation process into biogas so that the raw material becomes softer and decreased levels of lignin [7]. Early treatment will reduce the lignin compound in the lignocellulose due to the destruction matrix structure of lignocellulose [8]. Lignin is a substance which, together with the cellulose found in wood. Lignin is a polymer with aromatic structure formed from units Pénil related propane jointly by several different types of bonds. Lignin is difficult to degrade because of the complex and heterogeneous structure that binds to

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cellulose and hemicellulose in plant tissue. More than 30% of the crop is composed of lignin, which provides a solid form and provide protection against insects and pathogens [9].

Delignification process is done with the addition of microbes that can digest lignin thus decreasing the lignin contained in the raw material [10]. Pretreatment biology are considered to have the advantage and simplicity in a low capital investment more attractive [11]. Microbial consortium consisting of *Streptomyces sp*., *Geobacilus sp*., and *Trichoderma*. The function of microorganisms is doing delignification, reduce the degree of polymerization of the cellulose and hemicellulose hydrolysis. The addition of microbial consortium accelerate the degradation of cellulose, hemicellulose, and lignin into compounds needed by the microorganism biogas so that biogas production increased [7].

2 Materials and methods

This research is a kind of experimental research laboratories. The study was conducted at the Laboratory Waste Processing, Chemical Engineering, University of Diponegoro during the month of December 2016 - March 2017.

2.1 Content test TS rice straw

Analysis of total solids content (total solid / TS) by standard methods APHA

- The plate was dried at a temperature of 103-105 ° C for 1 hour, then cooled and stored in a desiccator until the cup is used.
- Weight the cup is weighed and recorded.
- Sample inserted into the cup as much as 25-50 g and weighed, then dried in an oven at a temperature of 103-105 ° C for 1 hour.
- Sample that has been dried and then cooled in a desiccators and weighed to the reduced weight 4% or 50 mg.

$$\% \, total \, solids = \frac{(A - B) \times 100}{C - B} \quad (1)$$

A = weight sample that has been dried + cup (mg)
B = weight cup (mg)
C = weight of the wet sample + cup (mg)

2.2 Pretreatment

- Took organic rice straw waste (biowaste), then conducted an examination of the total composition of solids and water content.
- The addition of acid is done by calculating the acid levels multiplied by the volume of the reactor is added with half the volume of water immersion chaff.
- Rice straw soaking for 24 hours.
- After soaking, chaff neutralized until the rice straw is no longer acidic
- Rice straw dried in the sun to dry.

2.3 Operational

- Rice straw has done acid pretreatment process is fed into the reactor in accordance with Table 1.
- Add water, enzymes, urea and rumen in accordance with Table 1.
- Wait for the fermentation process so that biogas formed.
- Measure the volume of biogas which is formed every two days until the biogas produced is not returned.

Table 1. Materials research

Variable	Microbial Consortium 5% v/v (ml)	Volume of water (ml)	Volume of Rumen (ml)	Rice Straw (gr)
1	10	76.61	76.61	46.77
2	10	76.61	76.61	46.77
3	10	76.61	76.61	46.77
4	10	76.61	76.61	46.77
5	10	76.61	76.61	46.77
6	10	76.61	76.61	46.77
7	10	76.61	76.61	46.77
8	10	76.61	76.61	46.77
9	0	76.61	76.61	46.77
10	0	76.61	76.61	46.77

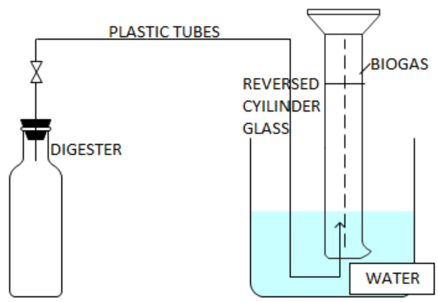

Fig 1. Schematic diagram of series laboratory batch assessment of SS-AD

3 Result and discussion

3.1 The Effect of Biological Pretreatment

Biological pretreatment aims to produce more hemicellulose and cellulose that help can be more widely available and easily digestible [6]. In this research using fixed variables microbial consortium of 5% of the total volume of liquid in the digester (200 ml). Then we get a volume of 10 ml. Biological pretreatment carried out after acid pretreatment. Biological pretreatment control variables used in the study, so there is no differences in the treatment of each study variable in terms of biological pretreatment.

3.2 The Effect of Acetic Acid Pretreatment

This study aimed to compare the biogas production between rice straw given early treatment with acidified with a solution of CH_3COOH with rice straw is not given early treatment. In addition, this study also compared two different levels of CH_3COOH to see the levels of acetic acid is optimum in the process of lignin degradation. Used CH_3COOH levels of 3 and 5% as a benchmark levels of acetic acid.

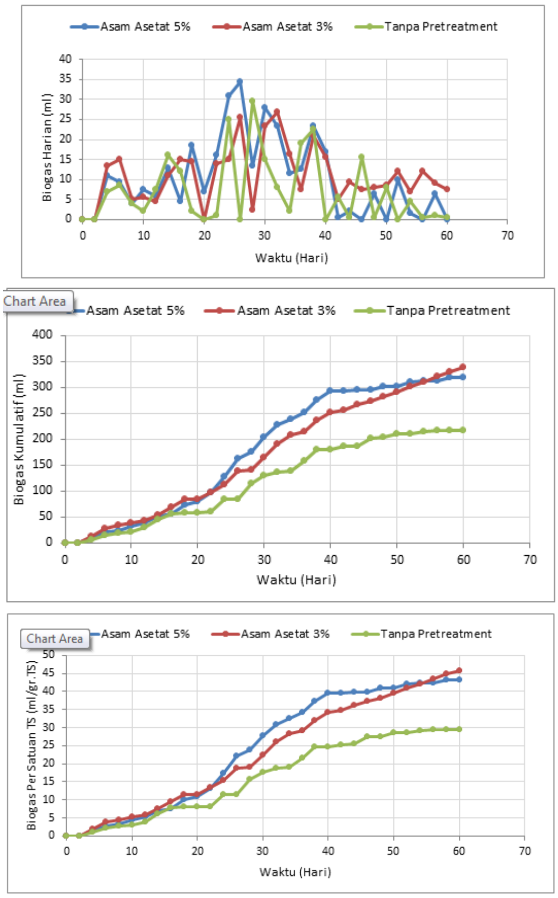

Fig 2. Biogas Productivity using Acetic Acid Pretreatment, (a). Daily Measurement, (b).The Cumulative Yield Biogas, (c). Cumulative/ TS

Acetic acid content of 5 and 3% with a concentration ratio of TS 21% compared to the levels of 3% tend to have a higher biogas yield than 5%. Total cumulative biogas yield per unit TS 3% acetic acid, 5% acetic acid, and without pretreatment respectively by 45.86; 43.28; and 29.51 ml.

Having an organic acid which is good potential to eliminate the inhibitory compounds such as lignin and cellulose structures are modified to be more susceptible to enzyme degradation [12]. The use of acid pretreatment mixture of acetic acid and propionic acid can significantly increase the production of methane up to 35.84% and approximately 34.19% can make the process of degradation of lignin, in addition as many as 21, 15% degree of hydrolysis obtained with 0.75% mol / L in the pretreatment for 2 hours with the liquids versus solids ratio of 1:20 (w / v) [13]. Treatment using a weak acid such as acetic acid at low concentrations can reduce the lignin content during the immersion process lasts a weak acid solution.

3.3 The Effect of Nitric Acid Pretreatment

This study aimed to compare the biogas production between rice straw given early treatment with acidified with HNO_3 solution with rice straw is not given early treatment. In addition, this study also compared two different levels of HNO_3 to see the levels of nitric acid which is optimum in the process of lignin degradation. Used HNO_3 content of 3% and 5% as a comparison of the levels of nitric acid.

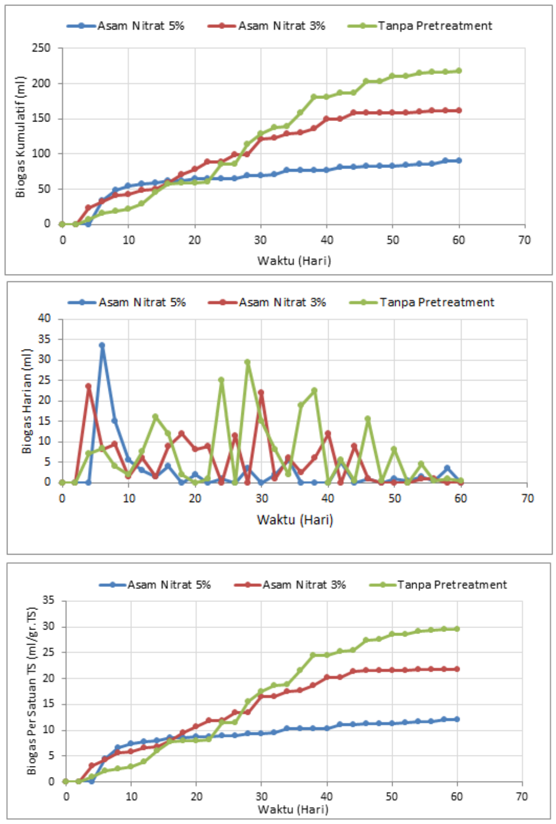

Fig 3. Biogas Productivity using Nitric Acid Pretreatment, (a). Daily Measurement, (b).The Cumulative Yield Biogas, (c). Cumulative/ TS

Nitric acid content of 5 and 3% with a concentration ratio of TS 21% compared to the levels of 3% tend to have a higher biogas yield than 5%. Total cumulative biogas yield per unit TS 3% acetic acid, 5% acetic acid, and without pretreatment respectively by 21.85 ml; 12.14 ml; and 29.51 ml.In research Tutt et al [7] suggest that nitric acid excellent in removing cellulose and hemicellulose, but generates byproducts that are difficult to be removed so that it has a greater negative impact on fermentation. Another study by Helle et al (14), states that the formation of by-products such as acetic acid during pretreatment which then inhibit the fermentation process. In the previous research explains that the process of delignification, the acid will cause the structure of lignin and hemicellulose which binds cellulose will be condensed and settles so that the cellulose will be free structure that is separate from the lignin and hemicellulose then will facilitate the access of enzymes or microorganisms to convert cellulose to be monomers sugar as a nutrient for fermentation biogas[15]. Liginin The decline is also accompanied by a decrease in hemicellulose and cellulose is the main nutrient that will use microorganisms to produce biogas that biogas obtained results will be slightly[13].

3.4 The Rate of Biogas Productioan from Rice Straw with SS-AD Methods

Assuming that the rate of biogas production in the biodigester is proportional to the specific growth rate of methanogenic microorganisms inside the biodigester. The rate of biogas production will follow Gompertz Equation[16]. This equation is a mathematical model for the observation time series, which is the slowest growth at the beginning and end of the period of observation that has the general shape as the following equation.

$$P = A.\exp\left\{-\exp\left[\frac{Ue}{A}(\lambda - 1) + 1\right]\right\} \quad (2)$$

P = cumulative biogas production, liter
A = maximum biogas production, liter
U = constants the maximum rate of biogas production (liter/hari)
λ =lag phase, day
t =cumulative time for biogas productivity, day
e = Euler Number (e = 2.7182...)

There is a constant influence on the kinetics of biogas production from acid pre-treatment using acetic acid 3 and 5%. Kinetic constant biogas formed by the pretreatment given 5% acetic acid are as follows, daily biogas production (A), biogas production rate (U), and the minimum time of formation of biogas (λ) respectively 45.5338 (ml / g TS); 1.5057 (ml / g TS.days); 11.3514 days. While the rice husk given acid pre-treatment using 3% acetic acid produces biogas as follows kinetic constant, daily biogas production (A), biogas production rate (U), and the minimum time of formation of biogas (λ) respectively 54.0824 (ml / g TS); 1.0593 (ml / g TS.days); 8,3152 days.

Table 2. Kinetic constants on Acetic Acid Pretreatment Effect on Biogas Production

Variable	A (ml/g TS)	U (ml/g TS.days)	λ (days)
CH_3COOH 5%	45,5338	1,5057	11,3514
CH_3COOH 3%	54,0824	1,0593	8,3152
Without Pretreatment	33,7254	0,8121	8,9317

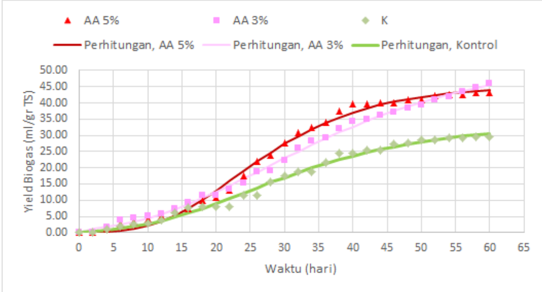

Fig 4. Relationship between Experiment data and calculation results on Effect of Pretreatment Research on Biogas Production Acetic Acid

There is a constant influence on the kinetics of biogas production from acid pretreatment using nitric acid 3% and 5%. Kinetic constant biogas formed with nitric acid pre-treatment given 5% is as follows, daily biogas production (A), biogas production rate (U), and the minimum time of formation of biogas (λ) respectively 10.7996 (ml / g TS); 0.6097 (ml / g TS.days); 0.1929 days. While the rice husk given acid pre-treatment using 3% nitric acid produces biogas as follows kinetic constant, daily biogas production (A), biogas production rate (U), and the minimum time of formation of biogas (λ) respectively 24.0036 (ml / g TS); 0.5759 (ml / g TS.days); 1.3080 days.

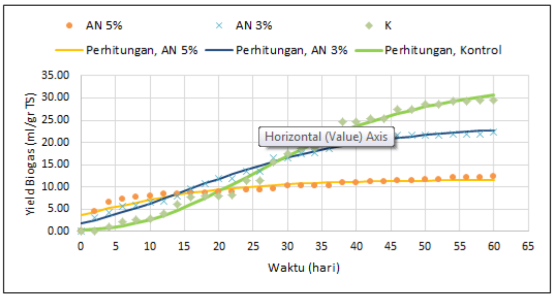

Fig 5. Relationship between Experiment data and calculation results on Effect of Pretreatment Research on Biogas Production Nitric Acid

After calculation by using the Polymath 6.0, known biogas production rate and can be seen on a day to stop what the biogas to produce biogas production. At 4:14 the picture shows the graphical form of biogas production rate with a variable yield acid pretreatment.

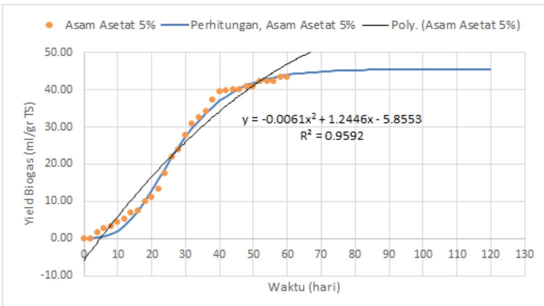

Fig 6. Calculation Result Data on Effects of Pretreatment Research Nitric Acid 5% of the Biogas Production

Calculation Result Data on Effects of Pretreatment Research Nitric Acid Production Biogas 5% against the trendline results obtained highest biogas yield on day 102 is equal to 57.63 ml / gr.TS. Then biogas productio further decline. While this is very different from the results of calculations using the Polymath 6.0, can be seen in Figure 4.15 that day all 118 results biogas yield reached the highest volume of 45.53 ml / gr.TS and constant or it can be said is not formed biogas.

Once the modeling is done on pre-treatment, namely by adding 3% CH_3COOH, obtained biogas yield of 45.86 ml / gr.TS. When there is a rice husk waste as much as one ton, it can produce biogas as much as 45.86 million ml or 45.860 m^3. If converted into other energy forms, obtain 1 m^3 of biogas equivalent to 4.7 kWh if it is converted into electrical energy. Then it can generate electricity capacity amounted to 215.54 kWh / day.

4 Conclusion

1. The preliminary treatment with acid 3% CH_3COOH produce biogas yield higher than 5% CH_3COOH and without pretreatment.
2. preliminary treatment without pretreatment acid generating biogas yield is higher than the pre-treatment HNO_3 HNO_3 3% and 5%.
3. The results of the biogas yield by pretreatment of organic acid (CH_3COOH) is better than the biogas yield results with pretreatment inorganic acid (HNO_3).
4. The biogas production rate in CH_3COOH 5% by value as follows: (A) as much as 45.5338 (ml / g TS); biogas production rate (U) of 1.5057 (ml / g TS.days); and the minimum time of formation of biogas (λ) is 11.3514 days.

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