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# Biogas production from bioethanol waste: the effect of pH and urea addition to biogas production rate

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***Abstract -*** Anaerobic treatment is a good choice to treat bioethanol waste due to the high concentration of COD content for producing biogas as renewable energy. The purposes of this study were to study the effect of addition nitrogen source and pH control to biogas production. The laboratory scale-anaerobic digestions used in this experiment were operated in batch system and at room temperature. In determination of optimum pH, bioethanol waste and rumen fluid fed into digesters with initial pH 6.0; 7.0 and 8.0. Influent COD : N ratio (in form of urea) used in this study was 700:7 in compare to control. The results showed that initial pH 7.0 produced the most biogas with total biogas 3.81 mL/g COD. While initial pH 6 and pH 8 had total biogas 3.25 mL/g COD and 3.49 mL/g COD respectively. At urea addition, biogas formed had 52.47% greater than that of at without urea addition (control variable). Controlled pH caused biogas was produced until 90-day investigation and might continue to be produced. Total biogas of control variable (without urea addition) and variable with ratio COD:N=700:7 influent were 11.07 mL/g COD and 11.41 mL/g COD respectively.

***Key words -*** bioethanol waste; biogas; initial pH; urea addition; pH control
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## INTRODUCTION

Energy and environment are the world's problems that are become analyzed together by researchers (Tejada and Gonzalez, 2006; Espinoza-Escalante et al., 2009; Abdullahi et al., 2011). The availability of fossil fuels such as oil, gas, coal has decreased while the consumption has increased because fossil fuels are nonrenewable energy. Rapid population growth and development of industrial areas led to the increasing energy demand. Besides that, burning of these fuels causes the global warming formation because $CO_2$is result of burning that is directly into the atmosphere. These problems, energy and environment, can be solved by production biogas from waste material.

Biogas is renewable energy that is produced by fermentation of organic materials under anaerobic condition in the digestion. Biogas contains 50-75% methane gas ($CH_4$) and 34-45% carbon dioxide ($CO_2$), and the other gases in small quantities are CO, $N_2$, $H_2$, $H_2S$, $O_2$ (Juanga et al., 2007; Karellas, 2010). Industrial wastewater such as vinasse can be feedstock of biogas because of its high chemical oxygen demand, COD more than 100,000 mg/L (Robles-Gonzales et al., 2010; Lutoslawski et al., 2011). In the anaerobic digestion, COD of organic materials is destroyed by microbial activity become methane gas ($CH_4$).

Vinasse is wastewater that is bottom product of distillation from production alcohol by fermentation. Beside containing high COD, vinasse has strongly acidic character (pH 3.67-4.98) (Siles et al., 2011; Lutoslawskiet al., 2011). So, vinasse can not be discharged directly into the river. If vinasse be discharged directly into the river, water biota will be death (Andreozzi et al., 1999). Some authors conducted research to find vinasse treatment solution in the alcohol industrial. Biologicaltreatment such as active sludge is expensive processing and produces poison during processing (Tang et al., 2007; Íñiguez-Covarrubias and Peraza-Luna, 2007). On the other hand, anaerobic treatment can destroy organic matter to biogas that can be used for heating at evaporation and distillation unit or can be saved for aerobic-anaerobic treatment (Wilkie et al., 2000).

Some authors studied treatment of vinasse in the anaerobic digestion. Espinoza-Escalantea et al. (2009) studied effect of pH to biogas production. At pH 6.5, biogas production is greater than pH 4.5 and 5.5. Buitron and Carjaval (2010) studied effect of temperature of anaerobic digestion to biogas production. At 35°C, biogas production is greater than 25°C.

Speece (1996) explained that at pH range 6.5-8.2 will produce biogas optimally. While, in the previous research just compared pH 6.5 with pH 4.5 and 5.5 which these pH don't include in the pH range 6.8-8.2. So, in this research studied effect of pH 6, 7, 8 to biogas production. Furthermore, enhancement of biogas production by urea addition and pH controlled was studied.

## MATERIALS AND METHODS

*Wastewater*

The wastewater used was vinasse obtained from an alcohol production. The alcohol industry located in Solo, Central Java, Indonesia, that produces alcohol from molasses. Table 1 lists the vinasse properties used as biogas feedstock.

**TABLE 1.**VINASSE PROPERTIES

| Parameters | Values |
|---|---|
| COD, mg/L | 279,527 |
| TS, % | 25.80 |
| pH | 3.1 |
| N, mg/L | 1,700 |

*Experimental set up*

Anaerobic digesters were made from two kinds of polyethylene bottle which have a volume of 600 mL and 5 liters. The bottles were plugged with rubber plug and equipped with valve for biogas measurement. Anaerobic digesters were operated in batch system and at room temperature. Biogas formed was measured by liquid displacement method as also has been used by Yetilmezsoy and Sakar (2008) and Budiyono et al. (2010a, 2010b). The anaerobic digestion of experimental laboratory set up as shown in Figure 1.

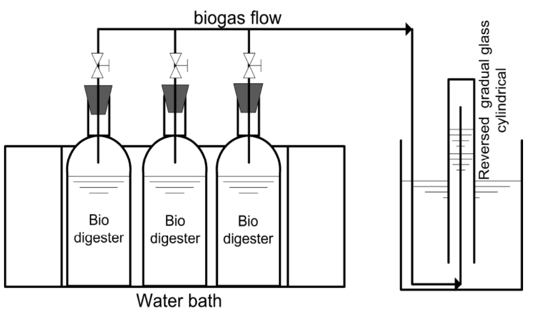


Figure 1. The batch anaerobic digestion of experimental laboratory

*Experimental design*

*Determination of optimum pH*

Anaerobic digestions of experimental laboratory using 600-mililiter volumes were operated in batch system. 250-mililiter vinasses were put in the digester. Rumen fluid as methanogenesis bacteria provider added into the digester as much as 10% v/v vinasses. Furthermore, pH initial was adjusted at 6, 7, 8 on each digester. pH variation of digestion influents as shown in Table 2.

**TABLE 2.**COMPOSITION AND PH OF DIGESTER INFLUENTS

| Composition of influents | pH influents |
|---|---|
| Vinasse+Rumen | 6 |
| Vinasse+Rumen | 7 |
| Vinasse+Rumen | 8 |

Parameters measured were biogas production daily and pH profile daily until biogas produced no more. pH condition which produced is the most biogas would use in the study effect of pH controlled to enhancement of biogas production from vinasse.

*Study urea addition and pH controlled to enhancement of biogas production*

In this study, pH initial was adjusted which produced is the most biogas in the *determination of optimum biogas*. Anaerobic digesters (volume 5 L) were operated in batch system. 1-liter vinasses and 10% v/v vinasses of rumen fluid were put into digesters.

From Table 1, can be known that ratio COD:N vinasse is 1150:7. Whereas ratio COD:N is optimum to produce biogas at range 350:7 – 1000:7. So in this experiment, the influent was adjusted ratio COD:N = 700:7 by urea addition. Its biogas production was compared with biogas production from influent without urea addition. Besides that, pH was controlled constant during biogas formed by NaOH addition that was studied to know its effect to biogas production. The variables in this study can be seen in Table 3.

*Experimental procedures*

Biogas formed was measured once in two days to know biogas production. pH subtracts in the digester were measured by pH meter every once in two days to know pH profile daily. COD influent and effluent of substrate were measured by COD meter to know % COD removal.

**Table 3.**Variation of composition (COD:N) and condition operation (pH)

| Composition of influents | COD:N | pH |
|---|---|---|
| V+R (Control) | 1150:7 | (NCC)) |
| V+R+U | 700:7 | (NCC) |
| V+R (Control) | 1150:7 | (CC) |
| V+R+U | 700:7 | (CC) |

Remarks: V, vinasse; R, rumen; U, urea; NCC, Not Controlled Constant; CC, Controlled Constant; COD:N, Ratio between chemical oxygen demand and nitrogen in the influent.

## RESULTS AND DISCUSSIONS

*The influence of pH influents to biogas production*

In the anaerobic digester, pH condition is important parameter because affects bacteria activity to destroy organic matter to biogas. pH optimum has range 6.5 – 8.2 (Speece, 1996).At pH 7, biogas formed was more bigger than pH 6 and pH 8. That was caused biogas production increased drastically in the first four days. From Fig. 2 (a) and (b), known that biogas was very significant at beginning of fermentation up to fourth day. However, on sixth day to twelve day, biogas production was decreasing. Biogas production was completely discharged at eighteenth day. pH of substrate decreased generally at the beginning fermentation until ending fermentation (Fig. 2.c).

At pH 6, the biogas production rate was lowest. So, the biogas cumulative production was also lowest. Whereas at pH 8, biogas production was still increased until $8^{th}$ day and was decreased until day twenty-two, then discharged at day twenty-four. From Fig. 2 (a), at pH 8 known that biogas production daily after sixth day had more than at pH 6 and pH 7. However, in the first four day, biogas production daily at pH 7 condition had more than at pH 6 and pH 8.

From Fig. 2 (c), known that profiles pH from beginning fermentation until ending fermentation at pH initial 6, 7 and 8 have the same pH profile. So, the most influential at the first time where bacteria adapted to pH condition substrate (in the first two days). This can be concluded that pH condition 7 causes bacteria evolves well in the digester. Some authors explained that the influence change in pH was very sensitive to bacteria activity in anaerobe fermentation. pH neutral with range 6.9 – 7.3 (Metcalf and Eddy, 2003); 6.4-7.6 (Anderson and Yang, 1992); 6.5-8.5 (Speece, 1996) could produce biogas highly. From these reports, among pH initial of all variables can be concluded that the pH initial 7 included in these range.

The drop of pH was caused acidogenesis bacteria produced acetate, hydrogen gas, carbon dioxide, and few other VFA such as propionic and butyric acid. A low pH value inhibited the activity of microorganisms involved in the biogas production especially methanogenic bacteria (Vicenta et al., 1984; Speece, 1996). Elbeshbishy and Nakhla (2012) explained that hydrogen ions caused pH low. A low pH related to the accumulation of VFAs that was toxicity for methanogenic bacteriain the digesters.

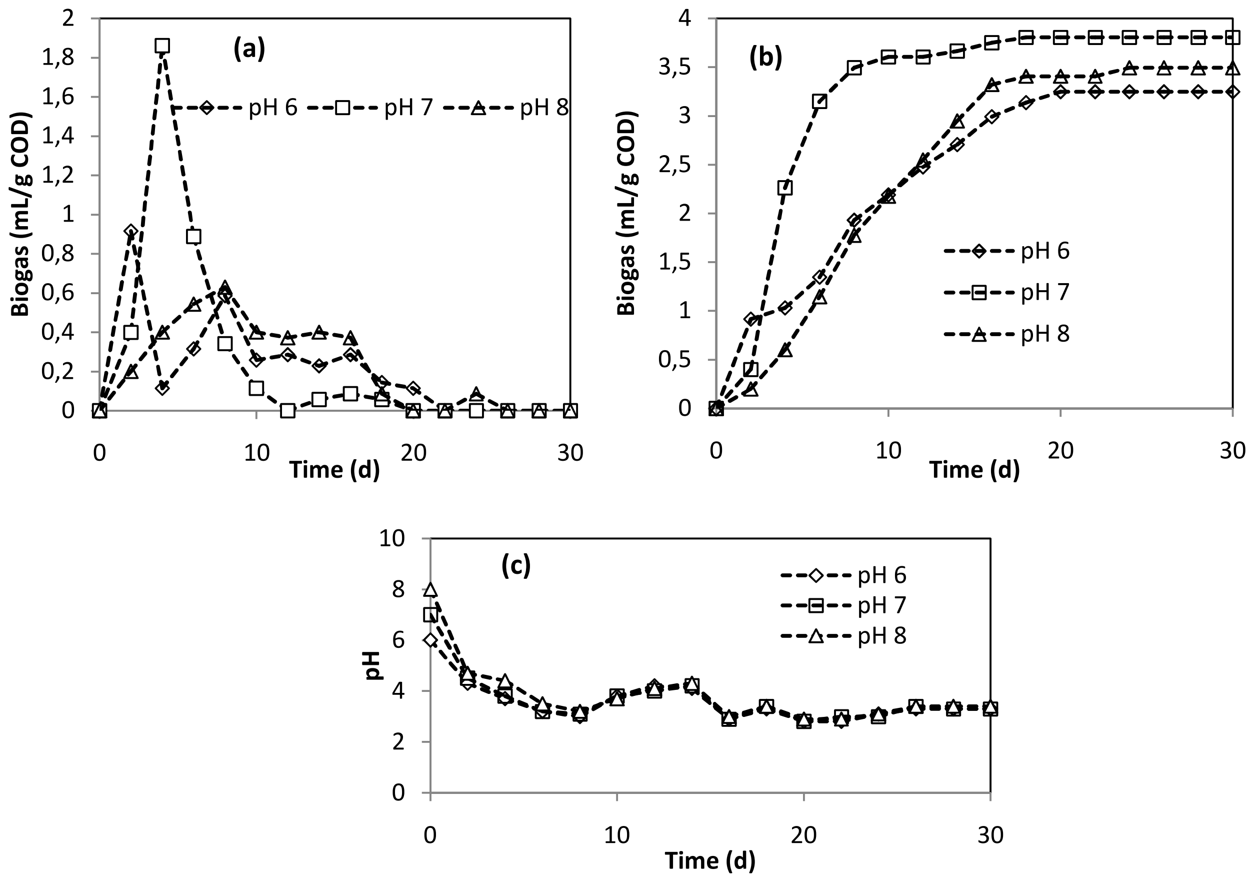


**Figure 2.** Biogas production daily (a); biogas production cimulative (b); pH profile (c) at pH condition 6, 7 and 8. Volume of anaerobic digester was 250 mililiters

The decrease in the pH could be due to the rapid VFAs production at substrate vinasse destroyed. In the alcohol production, molasses were hydrolyzed and fermented by *Saccharomyces cerevisiae*. Furthermore, alcohols formed were separated by distillation and bottom product of distillation was vinasse. So, vinasses contain the short chain molecular compounds. If vinasses were destroyed to biogas, biogas would be produced without through hydrolyze phase but directly to acidogenesis phase. In the acidogenesis phase, the short chain molecular compounds were changed to VFAs. Accumulation of VFAs made pH substrate decreased (Fig. 2 (c)).

*The influence of controlled pH to biogas production*

In the anaerobic digestions, the pH is a very important parameter. The influence change in pH was very sensitive to fermentation processing by bacteria activity. So, pH control is important for application in biogas production (Lutoslawski et al., 2011; Speece, 1996).

From Fig. 3 (a) and (b) can be known that pH control increased the biogas production. Biogas productions at pH control for control variable and COD:N=700:7 variable were 11.0754 ml/g COD and 11.4067 ml/g COD respectively. While at no pH control biogas productions were 2.2781 ml/g COD and 3.4733 ml/g COD respectively. At no pH control, pH substrate decreased so drastically that biogas production decreased. Decrease in pH substrate caused by accumulation of VFAs for the production of biogas (Fig. 3 (c)).

Lutoslawski et al.(2011) reported that biodegradation at pH control caused the final number of microbial cell total in the digester was more than process with no controlled pH. The controlled pH contributed largely to rate of degradation by microorganisms. In this experiment, pH control 7 caused methanogenic bacteria involve well in the bio-digesters. COD of substrate was destroyed by methanogenic bacteria to biogas. Biogas production at pH control formed until on ninety day and may still formed until the COD discharged (Fig. 3 (a) and (b)). Lutoslawski et al. (2011) reported that COD removal substrate at pH control was more than COD removal at no pH control.

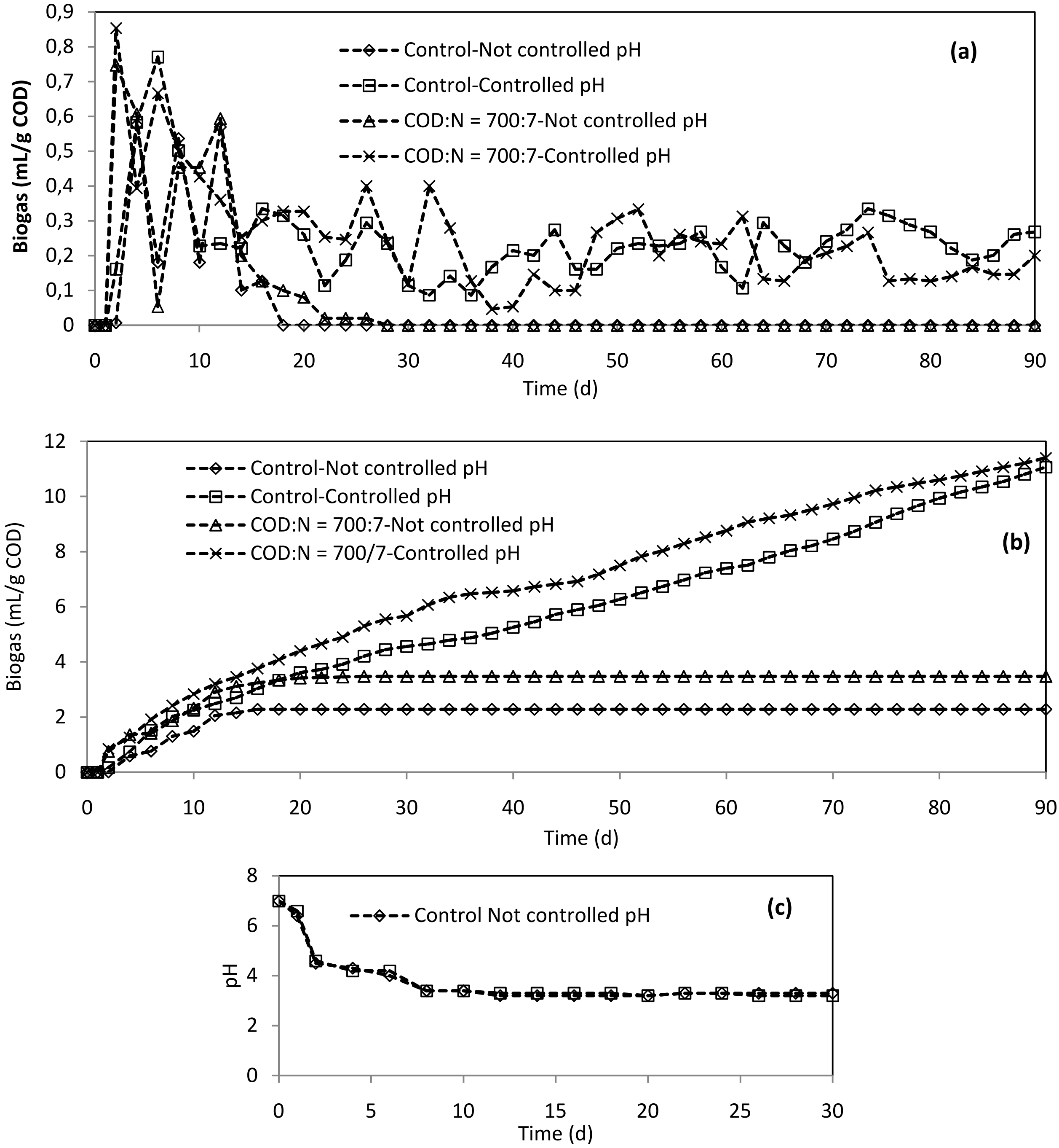


**Figure 3.** Influence urea addition and pH controlled constant to biogas production. Biogas production daily (a); biogas production cimulative (b); profil pH at not controlled pH substrate. Volume of anaerobic digester was 5L. InfluentspH were adjusted 7 for all variables.

*The influence of urea addition to biogas production*

Besides pH, the availability of nitrogen in the substrate is influential parameter that effects production of biogas. Anaerobic microbe needs nutrient for growing and evolving such as nitrogen. If availability nitrogen is too small in substrate, the bacteria will not synthesize the substrate that contains carbon. On the other hand, if availability nitrogen is too much, the growing of bacteria will be hampered because nitrogen will be released in form of ammonia (Soubes et al., 1994). Speece (1996) reported that wastewater containing COD would be destroyed and produced biogas optimally if substrate contained ratio COD:N in the range 350:7 – 1000:7.In this experiment, vinasse used had ratio COD:N = 1150:7. So, urea was added to make ratio COD:N of substrate 700:7.

Biogas formed was 52.47% greater than that of at without urea addition (control variable) (Fig.3 (a) and (b)). At urea addition, biogas was produced until 26 days then was discharged. Whereas in variable control, biogas was produced until 16 days then was discharged at 18 days. Addition of urea (COD:N = 700:7) effects biogas production that was more than control variable.Treatment pH control increased total biogas production of variable added urea that was 11.42 mg/L substrate. While, variable added urea without pH control had total biogas production 3.47 mg/L.

## CONCLUCIONS

The optimum pH resulted the higest biogas was pH 7. The controlled pH could increase total biogas formed i.e from 2.2781 to 11.0754 ml/g COD for variable control and from 3.4733 ml/g COD to 11.4067 ml/g COD. Urea addition could increase total biogas formed. The formed biogas was 52.47% greater than that of at without urea addition (control variable).

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