MICROCONTROLLER BASED HYDROGEN SULFIDE (H$_2$S) MONITORING IN BIOGAS SYSTEM

Diah Yuniarti$^1$, Sariyja$^2$, Ambar Pertuwiningrum$^3$

$^1$Kementerian Komunikasi dan Informatika, Jakarta
$^2$Jurusan Teknik Elektro dan Teknologi Informasi, Fakultas Teknik, Universitas Gadjah Mada
$^3$ Jurusan Ilmu Hewan dan Industri, Fakultas Peternakan, Universitas Gadjah Mada

*Correspondence: life.fillium@gmail.com*

Abstract

Energy issue, particularly related to fossil fuel, is one the main issues today. Biogas is a new and renewable energy issued in National Research Agenda (ARN) 2010-2014 to overcome the energy crisis problem. A so called purification process is used to remove contaminants in biogas, including H$_2$S in order to improve the standard requirement of biogas application. In this research, H$_2$S concentration in biogas system is measured and monitored by H$_2$S monitoring system. The hardware system comprises of piping and microcontroller AVR 8535 systems while the software system comprises of codes written in Delphi 7.0 and Code Vision AVR Eval. The result of the system is displayed on LCD or computer to enable the monitoring process by operator. The monitoring of H$_2$S sensor responses will be carried out for recycled BFA size of 60+100 mesh and -200 mesh. Experiment has been conducted for sensor warming up time and response time for H$_2$S and CH$_4$ sensor, calibration process for H$_2$S sensor and filter column. Based on sensor calibration experiment, transfer function of TGS825 sensor from calibration is $y = 0.0203x + 27.153$. The best adsorption model which represents BFA adsorption of biogas from tofu waste in the research is Thomas model.

1. Introduction

Energy issue, particularly related to fossil fuel, is one the main issues today. The depletion of oil reserve in the world has encouraged alternative energy research and innovation on fossil fuel substitution or complementary. Biogas is a new and renewable energy issued in National Research Agenda (ARN) 2010-2014 to overcome the crisis energy problem.

Biogas is the product of anaerobic digestion of organic matters composed mainly of methane (CH$_4$) and carbon dioxide (CO$_2$), with smaller amounts of water vapor and trace amounts of hydrogen sulfide (H$_2$S), and other impurities. Hydrogen sulfide is typically the most problematic contaminant because it is toxic and corrosive to most equipment. Additionally, combustion of H$_2$S leads to sulfur dioxide emissions, which have harmful environmental effects. Removing H$_2$S as soon as possible is recommended to protect downstream equipment, increase safety, and enable possible utilization of more efficient technologies such as micro turbines and fuel cells (Zicari, 2003).

A so called purification process is used to remove contaminants in biogas, including H$_2$S in order to improve the standard requirement of biogas application such as heating (boiler) and fuel of internal combustion engine. Thus, the monitoring of H$_2$S concentration in biogas is vital to ensure the biogas purification system performance in producing standard requirement of H$_2$S concentration for certain applications.

In this research, H$_2$S concentration in biogas system is measured and monitored by H$_2$S monitoring system. The system comprises of hardware and software combined together. The hardware system comprises of piping and electronic microcontroller elements while the software system comprises of codes written in Delphi 7.0 and Code Vision AVR Eval. The monitoring system is carried out by placing H$_2$S sensor in the biogas system. Output of the sensor, measured as analog voltage, is processed by ADC in the microcontroller. The result is displayed on LCD or computer to enable the monitoring process by operator. The monitoring of H$_2$S sensor responses will be carried out for BFA size of 60+100 mesh and -200 mesh which are recycled. Recycling process of BFA is conducted by reheating BFA in an oven with temperature 110°C for four hours. The experiments are conducted for sensor warming up time and response time for H$_2$S and CH$_4$ sensor, calibration process for H$_2$S sensor and filter column. At the end, the adsorption model represent adsorption of BFA size variables among Adam Bohart’s, Thomas’s and Yan’s are compared and analyzed.

2. Research Methodology

H$_2$S Monitoring System Design

The research location is at tofu waste biogas installation in Seyegan, Sleman, Yogyakarta. H$_2$S monitoring system comprises of H$_2$S measurement plant and H$_2$S electronic system. The filter column to purify biogas from bio digester is made of PVC with diameter 2.5” and height 30 cm. Biogas output from filter column flow through measurement plant. The piping configuration was established to enable biogas flow rate adjustment accordance to experiment requirement. Biogas from bio digester or the filter passes PVC tee connector and manual valve. After adjusting the flow rate through manual valve, biogas will pass through ¼” plastic connector and 1” PVC pipe. CH$_4$ sensor, H$_2$S sensor, and temperature and humidity sensor are placed in the end of PVC pipe. The monitoring system is displayed on computer to enable the monitoring process by operator.
Sensor calibration process is conducted by connecting the biogas output from the measurement plant to a plastic bottle with volume of 600 ml. The plastic bottle is filled by water up to half part of the bottle. Two orifices on the bottle are made to create input and output side to put plastic pipe. The input and output side of the plastic bottle is connected to the measurement plant. System diagram of sensor calibration is given in Figure 5.

The plastic bottle filled by water is used in the experiment to detain quick rate of H$_2$S concentration rate of biogas. After biogas flowing through the plastic bottle filled by water, its temperature and humidity relatively constant. Biogas coming out from the column attached with sensors is taken as sample. The sampling is taken by BalaiBesarTeknikKesehatanLingkunganandPemberantasanPenyakitMenularYogyakarta (BBTKL Yogyakarta) official. They also prepare the sampling equipment. Then, sampling result is compared to result from H$_2$S sensor of the monitoring system. The sampling process rate is slower than the reading by sensor. Thus, means of two nearest value of sensor reading is compared to single value of sample taken. Beside H$_2$S value, CH$_4$, temperature and humidity values are also taken online to support data analysis. Compressed air is used to normalize the sensor response after saturation condition caused by high concentration of H$_2$S of the biogas.

3. Results And Discussion

Experiment has been conducted for sensor characteristic, sensor calibration and filter column. Sensor characteristic experiments comprises of sensor warming up time and response time for H$_2$S and CH$_4$ sensor and calibration equation for H$_2$S sensor.

Sensor Warming Up Time

Sensor warming up time is time needed for the sensor system to reach stable output from its initial warming up. Warming up time experiments for H$_2$S and CH$_4$Sensor is given in Figure 6. The experiment is conducted in a normal atmosphere condition.
As seen in Figure 6, both H₂S and CH₄ sensors require several periods to be in their steady state condition from initial condition. The initial condition of the sensors is the condition before sensor supply is on. Thus, before the sensors can respond properly, warming process is necessarily required. Warming time required for H₂S sensor until it reaches its steady state is 32 minutes while CH₄ require less than 1 minute (41 seconds) to reach its steady state. In next experiments, the sensors are warmed for 1 hour.

Sensor Response Time

Response time is time needed for physical unit change measured. The sensor measurement process is started as the sensor responses in normal air condition. Afterwards, gas concentration is modified into larger value. It takes several periods for the sensor to reach its stable output after the gas concentration changing.

The experiment conducted by previously warm up H₂S and CH₄ sensors up one hour in a normal atmosphere condition. Then, after the voltage output value has relatively stable, a number of biogas is drained to the measurement plant. The voltage output changes occurred is plotted in a Delphi 7.0 graph as seen in Figure 7. and Figure 8.

H₂S Sensor Calibration

H₂S Sensor Calibration involves sampling taken by BBTKL. Transfer function equation of the sensor is analyzed by comparing the result between H₂S Sensor Reading and biogas sampling taken by BBTKL. The result is given in Table 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>H₂S Sensor Reading (ADC Value)</th>
<th>Voltage (mV)</th>
<th>BBTKL H₂S Sampling Result (ppm)</th>
<th>Tempe rature (°C)</th>
<th>RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>43</td>
<td>843.14</td>
<td>33.78</td>
<td>30.8</td>
<td>82</td>
</tr>
<tr>
<td>2.</td>
<td>104</td>
<td>2039.22</td>
<td>62.45</td>
<td>30.8</td>
<td>82</td>
</tr>
<tr>
<td>3.</td>
<td>109</td>
<td>2137.26</td>
<td>93.3</td>
<td>30.8</td>
<td>82</td>
</tr>
<tr>
<td>4.</td>
<td>226</td>
<td>4431.37</td>
<td>110.93</td>
<td>30.8</td>
<td>82</td>
</tr>
</tbody>
</table>

From H₂S sensor reading in mV and biogas sampling in ppm values as read in Table 1, a single equation line is created. Through linearization, approach equation of the line is obtained. The linear equation shows relation between H₂S concentration (ppm) and H₂S sensor output voltage (mV). Graphical data of the relation is given in Figure 9. The equation is:

\[ y = 0.0203x + 27.153 \]  

(1)
Microcontroller Based Hydrogen Sulfide ... (Diah Yuniarti, et al.)

Where $y = H_2S$ concentration (ppm) and $x = \text{sensor output voltage (mV)}$

Figure 9. Linearization of Voltage to Concentration from Sensor Calibration

Filter Column Experiments

Filter column experiments comprise of filter column I with recycled BFA aggregate size 60 + 100 mesh and filter column II with recycled BFA aggregate size -200 mesh. Before data recording of biogas characteristic from the filter output is taken, initial $H_2S$ concentration is measured by means of BBTKL sampling. The sampling result is given in Table 2.

Table 2. $H_2S$ Sampling Result of Biogas Filter Input by BBTKL

<table>
<thead>
<tr>
<th>No.</th>
<th>Biogas Filter Input Flow Rate</th>
<th>BBTKL $H_2S$ Sampling Result (ppm)</th>
<th>Temperature (°C)</th>
<th>RH (%)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5 L/m</td>
<td>117.73</td>
<td>30</td>
<td>82</td>
<td>Filter I Input</td>
</tr>
<tr>
<td>2</td>
<td>0.5 L/m</td>
<td>124.8</td>
<td>30</td>
<td>82</td>
<td>Filter II Input</td>
</tr>
</tbody>
</table>

The biogas output from the filter and sensor column is recorded by $H_2S$ monitoring system through Delphi 7.0 IDE. The display of recorded data for filter column I and filter column II are given in Figure 10 and Figure 11 respectively.

Figure 10. Recorded Data Display of $H_2S$ Monitoring System of Filter Column I

Figure 11. Recorded Data Display of $H_2S$ Monitoring System of Filter Column II

Filter Column I

From the voltage outputs of Figure 11, linear equation of $H_2S$ and $CH_4$ output voltage relative to time as seen in Figure 12 and Figure 13 respectively can be obtained.

Figure 12. Linearization of $H_2S$ Voltage Output Relative to Time

Figure 13. Linearization of $CH_4$ Voltage Output Relative to Time

Based on Figure 12 and Figure 13, linear equation of $H_2S$ and $CH_4$ Voltage Output are equation (2) and equation (3) respectively.

$$y = 4.7642x + 1040.9$$  \hspace{1cm} (2)

$$y = 2.0925x + 463.74$$  \hspace{1cm} (3)

Where:

$y = H_2S/CH_4 \text{ voltage output (mV)}$

$x = \text{time (s)}$

Online version available at http://journal.ugm.ac.id/index.php/ajse
Based on linear equation (1) of \( H_2S \) concentration (ppm) and \( H_2S \) output voltage (mV), conversion of \( H_2S \) sensor recorded data Figure 12 from \( H_2S \) voltage output to \( H_2S \) concentration can be obtained. Graphical data of the conversion is given in Figure 14.

![Figure 14. \( H_2S \) Concentration Relative to Time](image)

According to Table 2, initial \( H_2S \) concentration of the filter input is 117.73 ppm. Thus, after 360 s or 6 minutes, BFA has not reached its saturation condition. The BFA saturation time can be analyzed in linearization model of \( H_2S \) concentration graphics from Figure 14. The linearization model comprises of Adam-Bohart’s model, Thomas’ model, and Yan’s model, which are given in Figure 15, Figure 16 and Figure 17.

![Figure 15. Adam Bohart’s Linearization Model](image)

![Figure 16. Thomas’ Linearization Model](image)

Among three linearization model analyzed, the most appropriate model to represent experiment data of BFA size of 60+100 mesh is the model which has \( R^2 \) closest to value 1. It means that error between model equation and experiment data has the most minimum values. Based on Table 7, \( R^2 \) value closest to 1 is given by Yan’s linearization model. Thus, the best model used for BFA size of 60+100 mesh is Yan’s linearization model.

![Figure 17. Yan’s Linearization Model](image)

### Filter Column II

From Figure 12, As time running on, both voltage outputs of \( H_2S \) and \( CH_4 \) sensors are increasing but after the first minute, both \( H_2S \) and \( CH_4 \) voltage outputs are decreasing again. It occurred due to temperature and humidity changes. Meanwhile, linear equation of \( H_2S \) and \( CH_4 \) output voltage relative to time will be given for the first one minute of Figure 12 in Figure 18 and Figure 19.

### Table 3. Parameters of Adam Bohart’s, Thomas’, and Yan’s Linearization Model

<table>
<thead>
<tr>
<th>Model</th>
<th>( Co ) (mg/mL)</th>
<th>( Q ) (mL/s)</th>
<th>( \rho ) (g/mL)</th>
<th>Kinetic Constant ( (k_{AB}/k_{TH}/k_{Y}) ) mL/mg/s</th>
<th>Capacity of Column ( (q_{AB}/q_{TH}/q_{Y}) ) mg/g</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adam Bohart</td>
<td>0.118</td>
<td>8.333</td>
<td>0.526</td>
<td>0.014</td>
<td>1.083</td>
<td>0.837</td>
</tr>
<tr>
<td>Thomas</td>
<td>0.118</td>
<td>8.333</td>
<td>0.526</td>
<td>0.029</td>
<td>0.214</td>
<td>0.876</td>
</tr>
<tr>
<td>Yan</td>
<td>0.118</td>
<td>8.333</td>
<td>0.526</td>
<td>28.052</td>
<td>0.354</td>
<td>0.900</td>
</tr>
</tbody>
</table>
According to recorded data table obtained from the Delphi software, after BFA reaching its saturation condition at 60 s, temperature and relative humidity changes has occurred. Since the sensor output value is sensitive to humidity, although BFA has experienced saturation condition, H\textsubscript{2}S concentration tends to decrease. Thus, the linearization model will merely be analyzed from initial time up to saturation time at 60 s. Adam Bohart’s, Thomas’, and Yan’s linearization model of H\textsubscript{2}S concentration graph in Figure 20 are given in Figure 21, Figure 22, and Figure 23 respectively.

According to Table 2, initial H\textsubscript{2}S concentration of biogas filter input is 124.8 ppm. As seen in Figure 20, H\textsubscript{2}S concentration in the filter output is increasing from its initial starting time at 35.51 ppm up to 124.28 ppm or at 60 s. It means that BFA has reached its saturation condition several moments after 60 s. From 60 s, H\textsubscript{2}S concentration value is decreasing up to 127 s and increasing again afterward. According to recorded data table obtained from the Delphi software, after BFA reaching its saturation condition at 60 s, temperature and relative humidity changes has occurred. Since the sensor output value is sensitive to humidity, although BFA has experienced saturation condition, H\textsubscript{2}S concentration tends to decrease. Thus, the linearization model will merely be analyzed from initial time up to saturation time at 60 s. Adam Bohart’s, Thomas’, and Yan’s linearization model of H\textsubscript{2}S concentration graph in Figure 20 are given in Figure 21, Figure 22, and Figure 23 respectively.

Adam Bohart’s, Thomas’ and Yan’s linearization equation obtained from Figure 21, Figure 22 and Figure 23 respectively are:

\[ y = 0.0287x - 1.4548 \quad \text{(9)} \]
\[ y = -0.1232x + 2.2333 \quad \text{(10)} \]
\[ y = 2.4571x - 11.533 \quad \text{(11)} \]

Furthermore, equation (9), equation (10) and equation (11) and also data from Table 2 is used to find out parameter k\textsubscript{AD}, q\textsubscript{AD}, k\textsubscript{TH}, q\textsubscript{TH}, k\textsubscript{Y}, q\textsubscript{Y} of the linearization models. Parameters obtained are given in Table 4.
Table 4. Parameters of Adam Bohart’s, Thomas’, and Yan’s Linearization Model

<table>
<thead>
<tr>
<th>Model</th>
<th>Co (mg/mL)</th>
<th>Q (ml/s)</th>
<th>p (g/ml)</th>
<th>Kinetic Constant ($k_{sa}/k_{in}$)</th>
<th>Capacity of Column ($\rho_{sa}/\rho_{in}$)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adam Bohart</td>
<td>0.125</td>
<td>8.33</td>
<td>0.526</td>
<td>0.230</td>
<td>0.106</td>
<td>0.8562</td>
</tr>
<tr>
<td>Thomas</td>
<td>0.125</td>
<td>8.33</td>
<td>0.526</td>
<td>0.987</td>
<td>0.038</td>
<td>0.9098</td>
</tr>
<tr>
<td>Yan</td>
<td>0.125</td>
<td>8.33</td>
<td>0.526</td>
<td>164.069</td>
<td>0.011</td>
<td>0.6808</td>
</tr>
</tbody>
</table>

Among three linearization model analyzed, the most appropriate model to represent experiment data of BFA size of -200 mesh is the model which has R² closest to value 1. Based on Table 4.4, R² value closest to 1 is given by Thomas’ linearization model. Thus, the best model used for BFA size of -200 mesh is Thomas’ linearization model.

Analysis of Adsorption Capacity

From the analysis result of the best model for each BFA sizes, the best model which represents both BFA sizes can be chosen. According to AksudanGosen (2004), Thomas model is a solution that generally and widely used to solve column performance theory. Although the best model represents BFA size of -60+100 mesh is Yan’s model, according to Sarwono (2006), Thomas model is considered to have a strong correlation since its R² > 0.5 (RizkyTrianaPutri, 2012).

Adsorption capacity obtained from Thomas model in Table 3 and Table 4 for each BFA sizes is represented by $q_{in}$. The description can be seen in Table 5.

Table 5. Adsorption Capacity of BFA Variable Sizes

<table>
<thead>
<tr>
<th>BFA Size (mesh)</th>
<th>Initial Concentration (ppm)</th>
<th>Flow Rate (L/m)</th>
<th>Adsorption Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60+100</td>
<td>117.73</td>
<td>0.5</td>
<td>0.214</td>
</tr>
<tr>
<td>-200</td>
<td>125.8</td>
<td>0.5</td>
<td>0.038</td>
</tr>
</tbody>
</table>

Based on Table 5, it can be concluded that $q_{60+100 mesh}>q_{200mesh}$. Although BFA size of -200 mesh has smaller particle size than BFA size of -60+100 mesh, the initial $H_2S$ concentration of BFA size of -200 mesh is bigger than initial concentration of $H_2S$ concentration of BFA size of -60+100 mesh. A change in the inlet sorbet concentration affected the operating characteristics of the column. At low initial concentration, breakthrough occurred late and the treated volume is higher since the lower concentration gradient caused a slower transport due to decreased diffusion coefficient or mass transfer coefficient. The adsorbent gets saturated early at high initial concentration because binding sites become more quickly saturated in the system (Aksu and Gonen, 2004 in RizkyTrianaPutri, 2012).

4. Conclusions

Based on result and analysis of the research, conclusions obtained are given below:

1) Sensor characteristic experiments show that warming up time for $H_2S$ and $CH_4$ sensor is 32 minutes and 41 seconds respectively. Generally, sensor response time for both $H_2S$ and $CH_4$ sensors is less than 1 s.

2) Based on sensor calibration experiment, sensor output voltage is proportional with $H_2S$ concentration. The larger sensor output voltage, the larger $H_2S$ concentration.

3) Linearization of TGS825 sensor calibration result in following equation:

$$y = 0.0203x + 27.153$$

Where $y = H_2S$ concentration (ppm) and $x = sensor$ output voltage (mV)

4) Filter column I with BFA size of 60+100 mesh experiments give result:
   a. Linear equation of $H_2S$ and $CH_4$ Voltage Output
      $$y = 4.7642x + 1040.9$$
      Where $y = H_2S$ Voltage output (mV) and $x = time$ (s)
      $$y = 2.0925x + 463.74$$
      Where $y = CH_4$ voltage output (mV) and $x = time$ (s)
   b. The best model used for BFA size of 60+100 mesh is Yan’s linearization model with $R^2 = 0.9094$ and parameter $k_v = 28.052$ and $q_v = 0.354$, where $k_v$ is Yan Kinetic Constant (mL/mg/s) and $q_v$ = capacity of column (mg/g)

5) Filter column II with BFA size of -200 mesh experiments give result:
   a. Linear equation of $H_2S$ and $CH_4$ Voltage Output
      $$y = 100.03x - 398.08$$
      Where $y = H_2S$ voltage output (mV) and $x = time$ (s)
      $$y = 61.109x - 426.67$$
      Where $y = CH_4$ voltage output (mV) and $x = time$ (s)
   b. The best model used for BFA size of -200 mesh is Thomas’ linearization model with $R^2 = 0.9098$ and parameter $k_{th} = 0.987$ and $q_{th} = 0.038$, where $k_{th}$ = Thomas Kinetic Constant (mL/mg/s) and $q_{th}$ = capacity of column (mg/g)

6) The best model which represents BFA adsorption of biogas from tofu waste in the research is Thomas model. Besides generally and widely used to solve column performance theory, Thomas model in the research is considered to have a strong correlation since its $R^2 > 0.5$.

7) Adsorption capacity of BFA size of -60+100 mesh is higher that adsorption capacity of BFA size of -200 mesh.
mesh due to higher initial concentration of BFA size of 200 mesh compare to BFA size of 60+100 mesh.

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