Technology of Impurities Gas Elimination of Biogas to Produce Biomethane: A Mini Review

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Abstract

Biogas contains various gaseous components, such as CH\(_4\), H\(_2\)S, NH\(_3\), CO\(_2\), and H\(_2\)O. The higher CH\(_4\) content in biogas, the bigger energy content (caloric value). The H\(_2\)S, NH\(_3\), CO\(_2\), and H\(_2\)O contents are impurities gas in biogas that cause less in purity of CH\(_4\), thus biogas needs to be purified. The purification is in order to remove the impurities gas, moreover it can produce high purity of CH\(_4\) > 95\%, called biomethane. The integrated technology of condensation and two stages adsorption using activated carbon and zeolite can be used to purify biogas. This method is environmentally friendly because it does not produce secondary waste.

Keywords: Biogas; biomethane; elimination; impurities; integrated technology.

1. Introduction

Biogas is a renewable energy source that comes from anaerobic degradation of organic material by microorganism. It contains some gaseous components, the main components are methane (CH\(_4\)) about 54\% to 70\% and carbon dioxide (CO\(_2\)) 20\% to 45\%. Besides, it contains other gases in less of amount, they are hydrogen sulfide (H\(_2\)S), ammonia (NH\(_3\)), hydrogen (H\(_2\)), nitrogen (N\(_2\)), and water vapor (H\(_2\)O) [1]. If it is neither utilized nor managed, only released into ambient air, it can make air pollution since its contents as mentioned before. Air pollution is defined as entry or inclusion of substance, energy and other components into ambient air by human activities thus degrades the air quality to a certain level that causes the ambient air does not fulfill its function [2]. Utilization of biogas as energy source is an implementation of Regulation on Environment No. 32/2009.

Caloric value of biogas is about 500 BTU \(\cdot\) ft\(^{-3}\) to 700 BTU \(\cdot\) ft\(^{-3}\) (1 BTU equal 1 055 J) or 4 500 kcal \(\cdot\) m\(^{-3}\) to 6 300 kcal \(\cdot\) m\(^{-3}\) or 17 900 kJ \(\cdot\) m\(^{-3}\) to 25 000 kJ \(\cdot\) m\(^{-3}\) [3]. Energy content in biogas depends on methane concentration. The higher methane content in biogas, the bigger energy content is, or vice versa. Presence of the impurities of biogas causes reduction of methane purity, so that biogas needs to be purified to get high purity of methane and higher caloric value. Methane is a greenhouse gas, utilization of it in biogas means reduction of methane release to the atmosphere, which is good to inhibit global warming. People can also get the renewable energy source from biomethane.

Impurities of biogas besides reducing methane purity, they also have hazard toward human and environment. Hydrogen sulfide (H\(_2\)S) is colorless gas, smells like rotten eggs, at low concentration can be detected, irritant to eyes and respiratory tract. At medium concentration (150 mg \(\cdot\) L\(^{-1}\)) it will deactivate the olfactory nerve, as a result it is not detected. At concentration 300 mg \(\cdot\) L\(^{-1}\) or more, it is very dangerous if it is inhaled by human, it can cause death in several
minutes. Long term effects if people inhale it continuously at low up to medium concentration can cause dizziness, disturbed body balancing, and fatigue. It is corrosive to Cu, Cd, Hg, and metal oxide. If it is burned, it will be produced sulfur dioxide/sulfur trioxide (SO$_2$/SO$_3$) which is very corrosive and toxic. At the same time, it will form sulfuric acid (H$_2$SO$_3$) as a more corrosive compound [4]. Meanwhile, ammonia (NH$_3$) is colorless gas, pungent, irritant to respiratory tract, nose, throat, and eyes at concentration (400 to 700) mg $\cdot$ L$^{-1}$. When it contacts with eyes, it can cause blindness. Moreover, it can cause lung disorders and at 5 000 mg $\cdot$ L$^{-1}$ concentration, it can cause mortality [4]. Water vapor (H$_2$O) content can cause corrosion to metal equipment burners and give effect on lower caloric value of biogas when it is too much. Water vapor of biogas leads to slake the burning fire. The N$_2$ is inert and in a low concentration. Carbon dioxide (CO$_2$) is a greenhouse gas and one of the causes of global warming on earth based on Kyoto Protocol in 2007. Furthermore, CO$_2$ is one of the impurities which is pretty much in biogas, about > 30 %. The presence of CO$_2$ can affect caloric value of biogas, decrease the quality of biogas as gas fuel. Furthermore, in presence of moisture, it will form carbonic acid and may causes corrosion on metal equipment.

2. Material and Methods

2.1. Materials

The materials of this research are literatures (books and journals) and result of researches on impurities elimination technology of biogas.

2.2. Methods

The method used in this paper is literature review of results on impurities gas elimination technology of biogas researches. Moreover, the elimination technologies are evaluated to get which one is the best technology based on economic and environment comparison. Then, the development of elimination technology of every impurity can be made based on the evaluation

3. Result and Discussion

In general, elimination of impurities gas of biogas divided into four categories, i.e. adsorption, absorption, permeable through membrane, and water vapor content removal [5, 6, 7, 8]. Elimination technology of applied impurities gas of biogas has to consider environment aspect, a technology that does not cause secondary waste in its operation.

Adsorption technology is material accumulation process on interface between two phases. It is categorized into, chemical adsorption and physical adsorption [9]. Chemical adsorption is related to Langmuir equation whereas physical adsorption related to Freundlich equation as Eq. 1. Adsorbate in physical adsorption has a very weak bond, the interaction between adsorbate molecules just because of Van der Waals force [10], so that the physical adsorption is reversible and very easy to be separated between adsorbate and adsorbent. With these properties, when adsorbent has met its saturated point within a certain time then it can be regenerated so that it can be reused in adsorption process. There are many types of adsorbents, but the most widely used are activated carbon and zeolite.
Freundlich equation:

\[ Y = \frac{X}{M} = KC^{1/n} \]  

(1)

Where \( Y \) is amount of adsorbate per adsorbent mass (mg \cdot g^{-1}), \( X \) is adsorbate mass (mg), \( M \) is adsorbent mass (g), \( C \) is concentration (mg \cdot L^{-1}), \( K \) and \( n \) are constants. Value of \( Y, X, \) and \( M \) are

Eq. 1 above then plotted in a graph, it is forming a curve in Figure 1 below.

\[ Y = KC^{1/n} \]

**Figure 1.** Freundlich adsorption curve

\[ \text{Fin}. \text{ Cin} – \text{Fout}. \text{ Cout} = d(q.W)/dt \]  

(2)

Where \( \text{Fin} \) is flow rate of impurities gas in inlet (L \cdot min^{-1}), \( \text{Fout} \) is flow rate of impurities gas in outlet (L \cdot min^{-1}), \( \text{Cin} \) is concentration of impurities gas in inlet (mg \cdot Nm^{-3}), \( \text{Cout} \) is concentration of impurities gas in outlet (mg \cdot Nm^{-3}), \( q \) is amount of adsorbed impurities gas/adsorbent (mg adsorbate/gr adsorbent), \( W \) is mass of used adsorbent (g), and \( dt \) is change in adsorption time (min). From Eq. 2, the Freundlich equation is derived and meet Eq. 3 and Figure 2 is describe accumulation adsorption process.

\[ W.(dq/dt) + q.(dW/dt) = \text{Fin}.\text{Cin} – \text{Fout}.\text{Cout} \]  

(3)

**Figure 2.** Accumulation process of impurities in the adsorption column

Absorption is a diffusion gas particle transfer process into liquid \[8\]. The frequent used compounds in this process are water \[5, 7, 8\] and chemical substance (amine compounds) \[5, 7, 8, 11\] which can dissolve CO\(_2\) and H\(_2\)S. This technology has high removal efficiency (CH\(_4\) purity up to 99 %) because the impurities are soluble in the absorbent. This process has disadvantage, it produces secondary waste from amine compound that is used, while it needs
large volume of water if water is used as absorbent. So, this technology is less environmentally friendly.

Impurities gas removal using membrane is a separation process of CH$_4$ from H$_2$S, NH$_3$, and CO$_2$ gas using membrane as filter, principally [8]. Elimination of impurities gas using membrane technology is divided into two systems; single-stage and multi-stage system. In single-stage system, CH$_4$ purity can reach up to 97 %, whereas multi-stage system can meet CH$_4$ purity up to 99 % [5]. For application in Indonesia, this technology is less economical because the membrane used to purify gas still rarely produce in Indonesia.

Water vapor content removal is performed by condensation. In general, condensation is used as a pretreatment before purifying gas using another technology. Principally, in condensation process, when high temperature gas contacts with cooling media (usually use water), the heat transfer from gas to the media occurs and gas temperature decreases. It is caused the gas molecular kinetic energy will be diminished and gas molecules will move closer to each other (van der Waals force) which will cause the gas condensed to be liquid [11]. Water is the most widely used as cooling media in condensation [12]. Heat transfer in condensation can be analyzed by using heat balance as follows (Eq. 4).

\[
heat_{in} = heat_{out}
\]

\[
Q = m \times C_{pg} (T_{g1} - T_{dew\,point}) + (m \times \Delta H_{v}) = L \times C_{pL} (T_{l_{in}} - T_{l_{out}})
\]

(4)

where Q is rate of heat transfer (BTU · h$^{-1}$), m is rate of gas mass (lb · h$^{-1}$), L is rate of liquid mass as cooler (lb · h$^{-1}$), C$_{pg}$ is gas specific heat (BTU · lb$^{-1}$·ºF), C$_{pL}$ is cooler liquid average specific heat (BTU · lb$^{-1}$·ºF), T$_{g1}$ is gas temperature in beginning (ºF), T$_{lin}$ is cooler liquid temperature in inlet (ºF), T$_{lout}$ is cooler liquid temperature in outlet (ºF), Hv is condensation heat from steam (BTU · lb$^{-1}$) [(i) BTU equal to about 1 055 J, (ii) 1 lb is equal to 0.45 359 237 kg ].

In biogas purification, condensation aims to eliminate the moisture content (H$_2$O) to obtain dry gas. Gas drying process can also remove NH$_3$ [13]. The latest development of biogas purification technology is cryogenic separation. This technology principally utilizes the difference of condensation point of gas components in biogas. Biogas is chilled until the impurities gases are condensed or sublimed. Most of impurities gases can be condensed at -25 ºC [7], thus they can be separated from methane in liquid or solid fraction, whereas methane is accumulated in gas phase. The advantage of this technology is its ability to reach high purity of methane up to 99 %. However it needs many equipments to support it, especially compressors to compress gas to 40 bar (1 bar = 100 000 Pa), turbines, and heat exchangers, hence it is considered very expensive [8].

Other researcher has compared the economic and environmental aspects of some biogas purification methods [5]. The comparison based on data of investment and operating costs on each biogas flow rate in Europe as presented in Table 1, while the environmental aspect comparison is based on methane losses in Table 2.
Table 1. Economic aspect comparison of biogas purification methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Flow rate (Nm$^3$/h)</th>
<th>Investment</th>
<th>OC</th>
<th>Investment</th>
<th>OC</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CS</td>
<td>0.91</td>
<td>1.16</td>
<td>3.93</td>
<td>1.98</td>
<td>1.50</td>
</tr>
<tr>
<td>PS</td>
<td>0.91</td>
<td>0.99</td>
<td>2.60</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PSA</td>
<td>0.98</td>
<td>0.98</td>
<td>3.73</td>
<td>1.83</td>
<td>1.56</td>
</tr>
<tr>
<td>MS</td>
<td>0.87</td>
<td>0.93</td>
<td>1.67</td>
<td>1.70</td>
<td>1.1</td>
</tr>
</tbody>
</table>

WS: water scrubbing, CS: chemical scrubbing, PS: physical scrubbing, PSA: pressure swing adsorption, MS: membrane separation, OC: operating cost

From the table above, membrane separation has the lowest cost on its investment and operating cost. In Indonesia, membrane for gas purification is still limited production, thus it makes high cost in investment. According to this fact, membrane separation is not the most economical method in Indonesia.

Table 2 Environmental aspect comparison of biogas purification method

<table>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>WS</td>
<td>2</td>
<td>&lt;2</td>
<td></td>
<td></td>
<td>Medium</td>
</tr>
<tr>
<td>CS</td>
<td>0.04</td>
<td>&lt;0.1</td>
<td>0.03</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>4</td>
<td>&lt;2</td>
<td>13.75</td>
<td>High</td>
<td></td>
</tr>
<tr>
<td>PSA</td>
<td>2</td>
<td>2</td>
<td>5.5</td>
<td>Medium</td>
<td></td>
</tr>
<tr>
<td>MS</td>
<td>0.5–20</td>
<td>&gt;10</td>
<td>n/a</td>
<td>High</td>
<td></td>
</tr>
</tbody>
</table>

Comparison of environmental aspect which has been conducted [5], made based on methane losses of each method. Membrane separation has the biggest methane losses, since it also has high investment cost, it does not selected as the best method to purify the biogas.

Water scrubbing, chemical scrubbing, and physical scrubbing are classified into absorption process, because they use solvent. It was stated that water scrubbing, chemical scrubbing, and physical scrubbing can be regenerated by processing the solvent under high temperature and energy demand [16]. Physical scrubbing has high methane losses [18, 19], so it is not considered as an environmentally friendly method, although the solvent can be regenerated. Chemical scrubbing has the lowest methane losses and its cost is almost the same as pressure swing adsorption. But, it needs higher temperature than physical scrubbing [15] that considered as less environmentally friendly.

Based on the evaluation above, author found that adsorption or pressure swing adsorption is the most economical and environmentally friendly biogas purification method. Since biogas is a mixture of some gases, thus author evolves an integrated technology to eliminate the impurities gas. The selected processes are condensation to remove moisture/water vapor and then followed...
with adsorption to remove H$_2$S, NH$_3$, and CO$_2$. Adsorption can be carried out in two stages using activated carbon and zeolite (Figure 3).

Activated carbon is put after condensation to ensure the water vapor adsorption proceeds well. In condensation, usually the exit gas is dry, but when the water vapor is not condensed well, it can be adsorb by activated carbon. Zeolite can adsorb water vapor content, but it may reduce its adsorption capacity toward CO$_2$, since CO$_2$ is the highest impurities. So biogas adsorbed efficiency by zeolite is completely in dry state and CO$_2$ removal efficiency can reach optimum value. H$_2$S and NH$_3$ will be adsorpted by activated carbon.

Within a certain period of time, adsorbents will run into saturated condition, marked by unadsorpted impurities gas. It means that the concentration of impurities gases before adsorption process is equal with concentration after adsorption process. These saturated adsorbents can be regenerated to release adsorbates from pores of adsorbents, and they will be empty and open. Regeneration process can be classified into four categories, thermal swing, pressure swing, purge gas stripping, and displacement. Thermal swing is performed by increasing the temperature up from 400 °F to 600 °F, adsorbents may be heated directly or through fluid. Pressure swing is performed using vacuum to desorp adsorbents. Purge gas stripping is performed with purge gas to reduce partial pressure from adsorpted particles by high temperature and low pressure. Displacement is performed with a media that can be adsorpted by adsorbents to replace the adsorbates. Regeneration process selected based on technical and economical consideration is thermal swing method, where adsorbents only need to be heated.

4. Conclusion

Elimination technology of impurities gas of biogas to get high concentration of methane can be conducted by integrated technology of condensation and adsorption using activated carbon and zeolite. The result of this technology development will obtain biomethane, a sustainable and renewable energy source and environmentally friendly.
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References


