

CO₂ Absorption from Biogas by Glycerol: Conducted in Semi-Batch Bubble Column

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Abstract. Biogas is a renewable energy source that has been developed recently. The main contents of Biogas itself are Methane and carbon dioxide (CO₂) where Methane is the main component of biogas with CO₂ as the highest impurities. The quality of biogas depends on the CO₂ content, the lower CO₂ levels, the higher biogas quality. Absorption is one of the methods to reduce CO₂ level. The selections of absorbent and appropriate operating parameters are important factors in the CO₂ absorption from biogas. This study aimed to find out the design parameters for CO₂ absorption using glycerol that represented by the overall mass transfer coefficient (K₁a) and Henry's constant (H). This study was conducted in semi-batch bubble column. Mixed gas was contacted with glycerol in a bubble column. The concentration of CO₂ in the feed gas inlet and outlet columns were analysed by Gas Chromatograph. The variables observed in this study were superficial gas velocity and temperatures. The results showed that higher superficial gas velocity and lower temperature increased the rate of absorption process and the amount of CO₂ absorbed.

Keywords: Biogas; CO₂ absorption; Glycerol; Henry constant; The overall mass transfer coefficient

1. Introduction

The development of science and technology will be based on the increasing energy needs. This is demonstrated by the many development of renewable energy used to meet human needs. One of the renewable energy source that has a potential to be developed is biogas. At this time, the development of biogas utilization has been done by KESDM in 2015 through three schemes, namely through the state budget, semi-commercial biogas program ("Program Biru") and development of biogas-based power generation program by private sector [1].

The main content of the biogas are methane (CH₄) and carbon dioxide (CO₂). Some research on combustion characteristics has been proven that the presence of CO₂ in fuel combustion can reduce the rate of reaction. High CO₂ concentration in fuels can reduce its heating value and reduce the quality of biogas [2]. Common method that has been used in the refining process of biogas is absorption using



amine-based compound. However, this method has some constraints which are costly, corrosive, and high energy requirements for regeneration [3].

Based on the CO₂ gas separation scheme provided by Wahono in his journal namely “*Pemanfaatan Zeolit Lokal Gunung Kidul-Yogyakarta untuk Optimasi Sistem Biogas*”, the most appropriate method for biogas purification process by physical absorption [4]. Physical absorption is the absorption process of dissolved gas (solute) by physical interaction, diffusion of gasses into the water, or gas dissolving into the liquid phase without chemical reaction. Physical absorption process is primarily used when the concentration of dissolved CO₂ is high [5]. The main problem is high potential of solvent loss [3];[6].

One of the compounds that can be used as physical absorbents is glycerol. Glycerol has low vapor pressure, stable, non-toxic, cheap and available in vast quantities as a by-product of biodiesel production. According to Aschenbrenner and Peter in his Journal of Comparative Study of Solvent Properties for Carbon Dioxide Absorption, the terminal –OH have a higher affinity for CO₂ molecules that increase CO₂ absorption [7]. Dissolution of CO₂ in the glycerol caused by Van der Waals and electrostatic forces. The bond between the absorbent and CO₂ in the physical absorption is lower than the bond formed by chemical absorption [8]. Therefore, glycerol is possible to be used as an absorbent.

The aim of this study was to investigate CO₂ absorption by glycerol in semi-batch bubble column. Overall mass transfer and Henry’s constant are measured under various conditions. Parameters such as superficial velocity and temperature are varied.

2. Methodology/Experimental

2.1. Setup

The schematic diagram of CO₂ absorption in glycerol was performed in a semi-batch bubble column as shown in Figure 1. Glycerol (96%) was purchased from PT. Brataco. The simulated biogas (mixed gas) consists of 40% CO₂ containing N₂ was supplied by PT. Samator Gas. The liquid volume in the column was 250 ml. The column was immersed in a water bath to control the temperature of the liquid. Mixed gas supplied from cylinder and the gas flow rates were controlled by volume flow meters. For injection and uniform distribution of the gas phase, a gas sparger (sintered sparger) was installed at the center of bottom column. The concentration of outlet gas from the absorber was analysed with gas chromatography (GC). Range of gas superficial velocity from 0,56 cm/s to 0,73 cm/s and temperature from 293 to 333 K have been investigated.

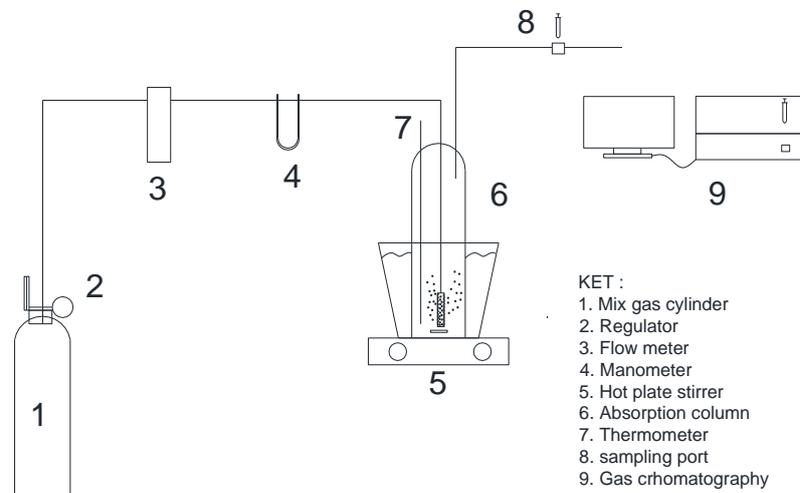


Figure 1. CO₂ Absorption Process Schematic Experimental Setup

2.2. Determination of $K_L a$ and H

Assuming that the liquid and gas are perfectly mixed, the carbon dioxide absorption process can be described by applying mass balance:

Mass balance of CO₂ in gas phase:

$$\frac{dC_{AG}}{dt} = \frac{1}{V \cdot \varepsilon_G} (C_{AGin} - C_{AG}) - \frac{K_L a}{\varepsilon_G} \left(\frac{C_{AG}}{H} - C_{AL} \right) \quad (1)$$

Mass balance of CO₂ in liquid phase:

$$\frac{dC_{AL}}{dt} = K_L a \left(\frac{C_{AG}}{H} - C_{AL} \right) \quad (2)$$

Where C_{AL} is the carbon dioxide concentration in the liquid phase, C_{AG} is carbon dioxide concentration in the gas phase and H is the Henry's constant.

For $K_L a$ and H value, the solution of equations 1 and 2 resulted C_{AL} and C_{AG} as a function of time. C_{AG} value calculation result is compared with C_{AG} research data. The difference between the calculation of C_{AG} and research data expressed by SSE (Sum Square of Error), Optimum $K_L a$ and H value has minimum SSE value. For superficial gas velocity variations and other temperature, the same calculation is carried out.

3. Results and Discussion

3.1. Effect of Temperature

To study and compare the effect of temperature, CO₂ concentration was measured at three different temperatures (293, 313 and 333K), all operation pressure is atmospheric pressure and inlet gas superficial velocity is 0.73 cm/s. Figure 2 shows that the increasing of temperature in the absorber lead to lower C_{AL} value in the solution. The lower C_{AL} value indicates the decrease of gas solubility in glycerol. At higher temperatures, the kinetic energy of molecules and the strength of their collision are larger [9]. The negative impact of temperature to solubility can be given a similar explanation [10]. CO₂ capacity of glycerol is optimum at 293K that is equal to 1.511 mol_{CO2} / L_{glycerol}.

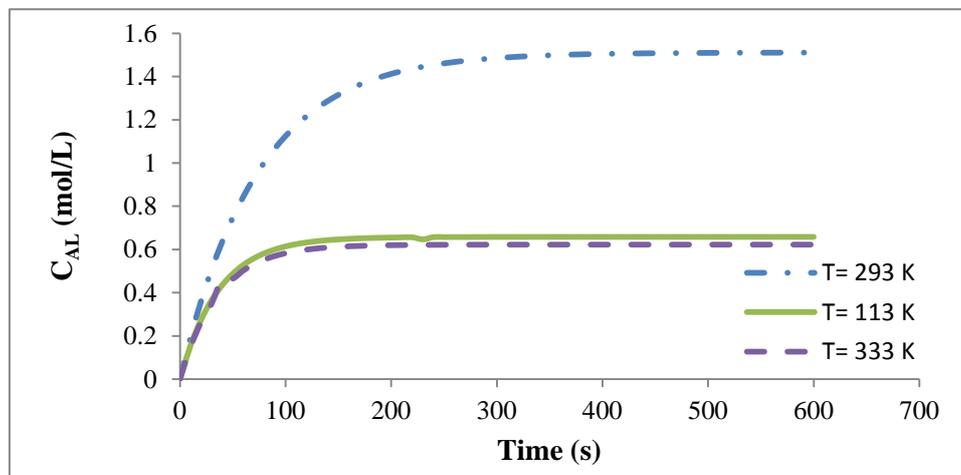


Figure 2. CO₂ Concentration in liquid phase (C_{AL}) Profile in Various Temperature (v_s=0.0073 m/s)

3.1.1. Henry's Constant. Table 1 shows the Henry's Constant for constant for CO₂ in glycerol at studied temperatures. As expected, the H value for CO₂ in glycerol increase along with the increasing temperature, due to the temperature is inversely proportional to gas solubility. The higher Henry's constant value means that the release of gas molecules from the liquid is easier [9].

Table 1. Henry's Constant Value of CO₂-Glycerol in Various Temperature

Temperature (K)	H (dimensionless)
293	0.0165
313	0.0289
333	0.0340

Henry's constant of experimental data at low pressure can estimated as a solubility in weight-fraction Henry's constant by Iwai [11].

$$H^* = \frac{P \cdot y_{CO_2}}{w_{CO_2}} \quad (3)$$

Table 2 shows the comparison of Henry's constant obtained both of calculation and the values obtained in the other absorbents.

Table 2. Henry's constant in various absorbent at different temperatures

H*(MPa)							
T(K)	This Work	T(K)	Selexol ^{[12],[13]}	sulfolane ^[14]	PEGME250 ^[15]	EGMEE ^[15]	Genosorb ^[16]
293	4.47						
303	7.1	298	3.6	8.7	9.5	10.3	10.3
313	8.77	313	4.7	11.1	10.8	10.8	10.8
333	11.85	333	6.5	15.8	13.3	13.9	13.9

3.1.2. Heat of Absorption CO₂-Glycerol. Heat of absorption is directly associated with the energy required to regenerate absorbent. Heat of absorption is also a significant factor to recycle the CO₂ in glycerol [17]. The enthalpy change that occurs when CO₂ gas absorbed into glycerol can be described using the Van't Hoff equation [18].

$$\ln(H) = \ln(H^0) - \frac{\Delta H_{\text{Abs}}}{R} \frac{1}{T} \quad (4)$$

The influence of temperature on Henry's law constant is present in Figure 3. that plot the natural logarithm of Henry's law constant to inverse temperature. Linearized equation of Equation 3 is $\ln(H) = 16,289 - 2278 \frac{1}{T}$. Based on the linearized equation, ΔH_{abs} value obtained from the slope of the Van't Hoff equation is -14.12 kJ/mol. Negative result shows that the process occurs is exothermic [16]. Based on the theory of Jaycock and Parfitt, the value of ΔH_{abs} (energy requirements) range in the physical processes is -20 kJ/mol to -0 kJ/mol. According to Jaycock and Parfitt theory, the process of CO₂ absorption by glycerol is physical absorption [19].

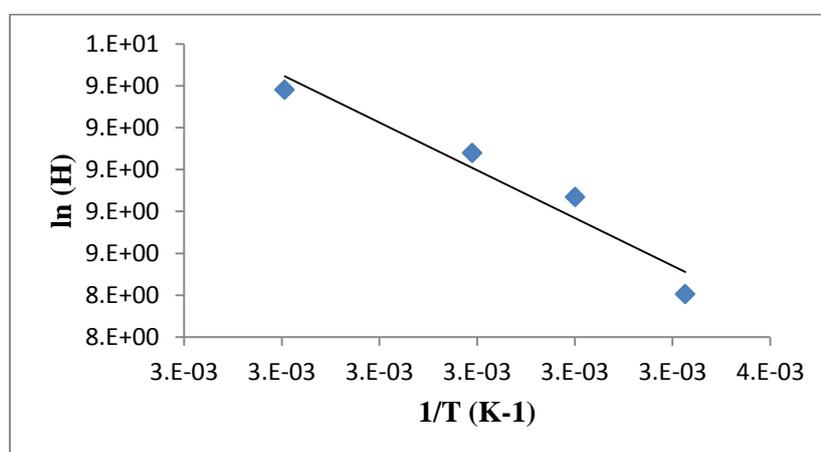


Figure 3. Dependence of Henry's law constant with temperature

The calculated values of heat of absorption for Glycerol-CO₂ system and other absorbent are given in table 3.

Table 3. Heat of Absorption CO₂ in various absorbent

No	Komponen	ΔH_{abs} (kJ/mol)
1	CO ₂ -Gliserol	-14.12
2	CO ₂ -MEG (Monoethyleneglycol) ^[9]	-11.77
3	CO ₂ -Propilenecarbonat ^[13]	-12.2
4	CO ₂ -selexol ^[13]	-14.3
5	CO ₂ -Genosorb 1753 ^[16]	-14.48
6	CO ₂ -water ^[20]	-12.72

3.2. Effect of Superficial Gas Velocity

To study and compare the effect of gas superficial velocity, CO₂ concentration was measured at three different gas superficial velocity (0.0056; 0.0062; and 0.0073 m/s), all operation pressure is atmospheric pressure and temperature is 303 K. Figure 4. shows that the concentration of CO₂ in the gas out in various superficial velocity increase throughout the absorption process. In superficial velocity of 0.0073 m/s, the constant concentration of CO₂ out from bubble column can be achieved more quickly compared to superficial velocity of 0.0056 m/s and 0.0062 m/s. This is possibly due to the amount of CO₂ gas that flows in the absorption column, so higher superficial velocity results high amount of CO₂ flowing and contact with the glycerol. Higher gas superficial velocity will increase the amount of CO₂ gas bubble dissolved into the glycerol. However, increasing of gas superficial velocity can increase the size of gas bubbles [21]. The Large size of gas bubbles will increase turbulence in the liquid phase, and also increase the flotation velocity [22].

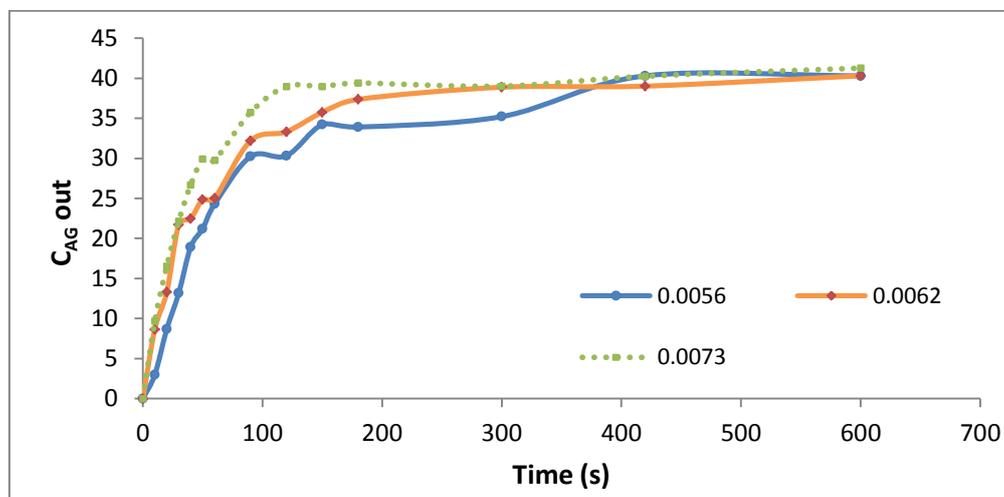


Figure 4. CO₂ Concentration Profile in Various Superficial Velocity (T=303K)

3.2.1. Mass Transfer Coefficient ($K_L a$). The gas-liquid mass transfer coefficient ($K_L a$) obtained in this study shows the magnitude of the mass transfer from the gas phase into the liquid in the absorption column. Figure 5. shows that the greater value of superficial velocity will increase the value of $K_L a$. According to Bouaifi, the increase of superficial velocity may increase the contact area between the gas and liquid and also $K_L a$ value [23]. For high superficial velocity, turbulence in the absorption column expressed by the Reynolds number (Re) will be even greater. High turbulence causes higher contact that occurs between the gas bubbles and fluid [24].

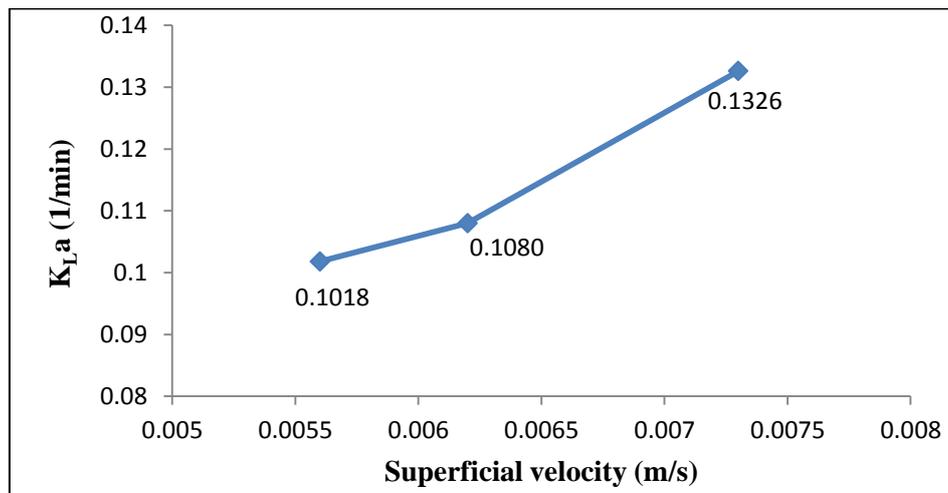


Figure 5. $K_{L}a$ Value to Gas Superficial Velocity ($T=303$ K)

The relations between Re numbers and $K_{L}a$ can be explained by the empirical approach in the form of dimensionless number [25]

$$Sh_L = \frac{K_L a d_p}{D} = 2 + b' Re_G^{0,779} Sc_L^{0,546} \left(\frac{d_p g^{\frac{1}{3}}}{D^{\frac{2}{3}}} \right) \quad (5)$$

The suitability of theoretical and calculations in this research is determined by calculating the relative error. Comparison $K_{L}a$ in this research and theoretical calculations are shown in Table

Table 4. $K_{L}a$ and $K_{L}a$ Hungmark Equation Value Comparison

Vs (m/s)	$K_{L}a$ (1/min)		Relative Error (%)
	Research Data	Hungmark, 1967	
0.0056	0.102	0.121	18.52
0.0062	0.108	0.130	20.78
0.0073	0.133	0.149	12.29

In Table 4 shows that the theoretical calculation error compared to data research superficial velocity range from 12% - 20%. These error values could give justification that optimization for parameter determination in mathematical model is completely acceptable.

4. Conclusion

In this study, glycerol as a new absorbent for CO_2 absorption bubble column has been studied. CO_2 absorption capacity of glycerol is $1.5 \text{ mol}_{CO_2}/L_{\text{glycerol}}$. Higher superficial gas velocity and lower temperature increased the rate of absorption process and the amount of CO_2 absorption. The relationship between the value of Henry's law constant toward the time followed the equation $\ln(H)=16.289 - (2278)/T$.

5. Acknowledgement

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