

The Explosion Severity of Biogas(CH₄-CO₂)/Air Mixtures in a Closed Vessel

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Abstract. Biogas which consists of methane (CH₄) and carbon dioxide (CO₂) could explode when diluted to a certain degree with air in the presence of ignition source. The maximum explosion overpressure (P_{max}), the maximum rate of pressure rise $(dP/dt)_{max}$, flammability limits, and deflagration index are the most important explosion severities parameters to characterize the risk of explosion. In this research paper, the effect of equivalence ratio (ER) of biogas/air mixtures and the effect of CO₂ concentrations presence in biogas were studied in a 20 L spherical vessel. The values of P_{max} and $(dP/dt)_{max}$ of biogas/air mixtures were more severe at ER 1.2. At various CO₂ content, P_{max} and $(dP/dt)_{max}$ of biogas/air mixtures were the least affected at 45% vol/vol of CO₂. On the other hand, deflagration index (K_G) of biogas/air mixtures trend was the most severe at 35% vol/vol of CO₂ content despite the lowest P_{max} and $(dP/dt)_{max}$ at 45% vol/vol of CO₂ content. The lowest values in P_{max} and $(dP/dt)_{max}$ were due to the diffusivity properties of CH₄ that had surpassed the CO₂ suppression effect. Furthermore, the presence of CO₂ in biogas/air mixtures had increased the upper flammability limit and lower flammability limit of biogas.

Introduction

The explosion propagation in a constrained area loaded with a combustible mixture raises essential protection issues for human-related activities such as fuel handling, transportation or storage. After the ignition, the fire propagates in the entire constrained area determining a quick energy release which followed by pressure rise, heat and light emission. The most critical data essential for design a pressure relief system or venting is pressure evolution during the explosion. In safety aspects to characterize the risk of explosion, the most important explosion severities parameters are the maximum explosion overpressure, (P_{max}), the maximum rate of pressure rise, $(dP/dt)_{max}$, flammability limit, and deflagration index, (K_G) [1].

The composition of biogas varies depending on the type of nature waste and processes and furthermore differs in time. However, the highest constituents in biogas composition are methane (CH_4) and carbon dioxide (CO_2). Both of these gases vary in proportions between 50-80% of CH_4 and 30-50% of CO_2 . Although biogas also contains traces of hydrogen sulfide (H_2S) and other compounds, the explosivity characteristic of biogas is not affected due to its small concentrations [2-5]. CO_2 is a substance which has difficulty to react [6]. In general, the presence of CO_2 in biogas has a negative impact on the normal burning velocity and maximum rate of pressure rise due to its extraordinary inerting potential [7]. The negative impact further leads to the reduction of flame temperature which ultimately affects the flammability limit of biogas [8].

Although the effect of CO_2 on CH_4 had been studied extensively by many researchers, none of the studies emphasized the effect of equivalence ratio (ER) and CO_2 concentration on biogas/air mixture. Therefore, the focus of this paper is to investigate the effect of ER on biogas (CH_4 - CO_2)/air mixture concentration and the effect of CO_2 concentration on the explosion severities parameters mainly P_{\max} , $(dP/dt)_{\max}$, flammability limit, and K_G of biogas/air mixture at initial ambient temperature and pressure.

Experimental Procedures

Materials

A series of tests were carried out to observe the explosion pressure development for different biogas-air mixture concentrations ranging from 9.6 to 18% vol/vol (or ER= 0.8 to 1.5). The effect of the CO_2 concentration in the biogas/air mixture was also varied from 30 to 45% vol/vol. In this study, biogas with 60% vol/vol CH_4 and 40% vol/vol CO_2 was used as a basis. Both gases of CH_4 and CO_2 with purity 99.9% were purchased from a local company.

Experimental Equipment

The experiment was carried out in a standard 20 L hollow sphere made of stainless steel which is manufactured by Adolf Kühner AG. The vessel is equipped with a water jacket, control unit, measurement, and control system, pressure measuring system, vacuum pump and an ignition device as shown in Fig. 1.

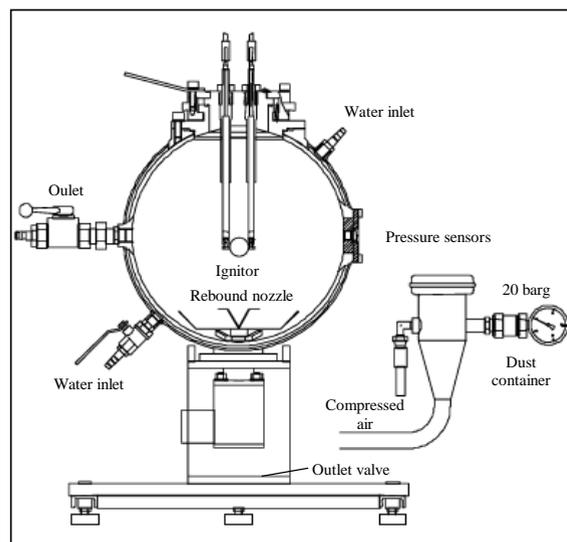


Fig. 1: Schematic diagram of the standard 20 L sphere.

Methods

Before the explosion test, the vessel was cleaned and vacuumed up to -0.8 bar. Chemical igniters (10 J energy) were then attached to the electrodes. The biogas/air mixture was prepared directly in the vessel according to the partial pressure method until reached the required mixture composition at a total pressure of 1.013 bar using a high precision digital pressure gauge. The mixture composition was controlled to an accuracy of 0.2 mbar (0.002% of the composition). The gases used were initially at ambient conditions (298 K and 1 bar). After the gases were added, the mixture was centrally ignited by a pair of electrodes with ignition energy of 10 J. The explosion overpressure was recorded by using two Kistler piezoelectric pressure sensors which are located on the measuring flange. Each experiment was made at ambient initial pressure and temperature (298 K and 1 bar) where a minimum of three experiments was performed for each of the conditions.

Result and Discussions

The Effect of Biogas/air Mixture Concentration on Explosion Severity

Fig. 2(a) and 2(b) present the P_{\max} and $(dP/dt)_{\max}$ of biogas/air mixture at various equivalence ratio (ER). The trends of P_{\max} and $(dP/dt)_{\max}$ increase as ER increases until reaches 1.2. Beyond the value of 1.2, the trends of P_{\max} and $(dP/dt)_{\max}$ decrease. The increase in both trends was due to the CH_4 composition in biogas that plays an important role to attenuate the burning rate since CH_4 has a very high specific heat capacity, which is almost 4 times higher than CO_2 . In addition, CH_4 is a fast diffusing reactant relative to the increase of the flame stretch towards the reactant (unburned gas mixtures) [9]. The properties of CH_4 have enhanced the overall mass burning rate. At lean concentration, ($\text{ER} < 1.0$), the small amount of CH_4 limits the stretch effect towards the reactant (unburned gas) which decreases the overall mass burning rate. At $\text{ER} < 1.2$, in a slightly rich concentration, the flame has highly diffusive-thermal stability which indicates the Lewis number close to 1 ($\text{Le} \approx 1$) [10]. At this instance, the flame is stretching towards the unburned gas, enhancing local heat release [10, 11] and giving a rapid increase in mass burning rate. At rich concentration ($\text{ER} > 1.2$), the insufficient oxidizer resulted in incomplete combustion, reducing the heat release and thus slowing down the burning rate [12, 13]. This could be the reason for the present observation in which the higher P_{\max} and $(dP/dt)_{\max}$ for both gases shifted to the slightly rich concentration ($\text{ER} = 1.2$). Therefore, biogas/air mixture at $\text{ER} = 1.2$ was more severe to about 1.8 (P_{\max}) and 6.7 ($(dP/dt)_{\max}$) time as compared to the lean concentration ($\text{ER} = 0.8$). Furthermore, from Fig. 2(a) and 2(b), it is clearly seen that both of the P_{\max} and $(dP/dt)_{\max}$ at $\text{ER} = 1.5$ is lower than $\text{ER} = 0.8$. This is because, at $\text{ER} = 1.5$, too much excess CH_4 was suspected diffused into the flame front. Since the amount of oxidizer presence in the mixture at $\text{ER} = 1.5$ is lower than $\text{ER} = 0.8$, less CH_4 is reacted with the oxidizer resulted in incomplete combustion. This causes the mass burning rate of the mixture at $\text{ER} = 1.5$ to be lower than the mixture at $\text{ER} = 0.8$ hence causing the P_{\max} and $(dP/dt)_{\max}$ at $\text{ER} = 0.8$ to be about 1.0 (P_{\max}) and 1.5 ($(dP/dt)_{\max}$) time higher as compared to the mixture at $\text{ER} = 1.5$.

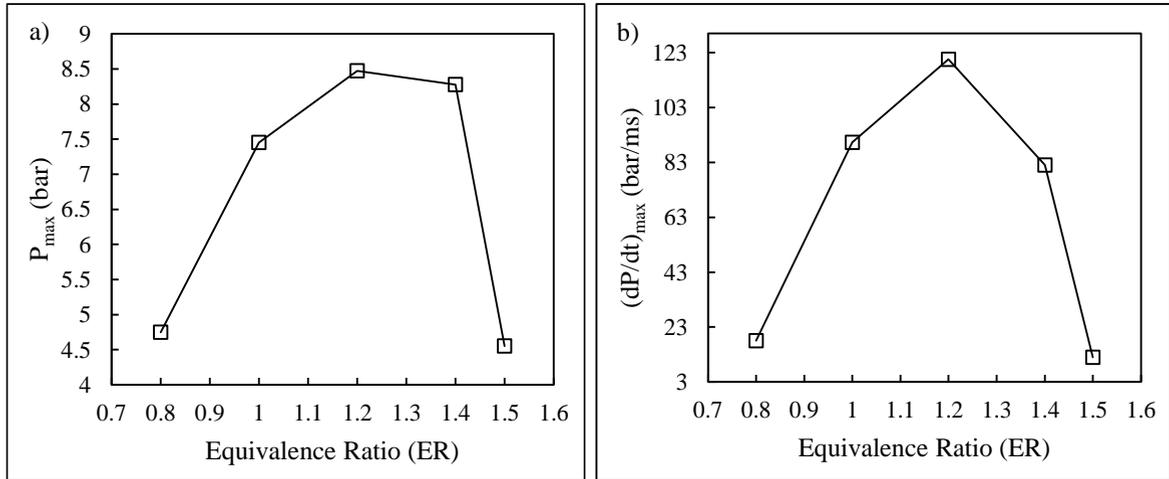


Fig. 2: Biogas/air mixtures at initial ambient temperature and pressure. (a) Effect of concentration on the maximum explosion overpressure. (b) Effect of concentration on the maximum rate of pressure rise.

The Effect of CO₂ on Biogas/air Mixture Explosion Severity

Fig. 3(a) and 3(b) show the effect of CO₂ concentration in a biogas/air explosion. 45% vol/vol CO₂ content in biogas gave the lowest effect to the P_{max} and $(dP/dt)_{max}$. The value of P_{max} was recorded at 7.7 bar while $(dP/dt)_{max}$ was at 82.2 bar/ms respectively. The same finding was reported by Mitu et al. [14] where the highest decrease of both P_{max} and $(dP/dt)_{max}$ occurred when CH₄ was blended with CO₂. According to Qin et al. [15], the presence of CO₂ in biogas is acted as a heat sink which had a tendency to absorb the heat during the combustion. Wang et al. [16] and Chan et al. [17] also reported that CO₂ had a better suppression effect that tended to reduce the flame temperature. Therefore, the presence of 45% vol/vol CO₂ in biogas has a greater ability to absorb the heat combustion. This phenomenon may change the flame stability [6, 18] and hence reduce the flame temperature that can lower the overall mass burning rate which reflects P_{max} and $(dP/dt)_{max}$. Hence, biogas containing 55% vol/vol CH₄ and 45% vol/vol CO₂ leads to the least effect on the explosion severity. Fig. 3(a) and 3(b) also show that both P_{max} and $(dP/dt)_{max}$ have a different trend at various CO₂ concentrations in biogas range from 30-40% vol/vol. The highest P_{max} approximately 8.48 bar was obtained at 40% vol/vol CO₂ while the highest $(dP/dt)_{max}$, 130 bar/ms was recorded at 35% vol/vol CO₂. The inconsistent result may be due to the chemical properties of CH₄ and the kinetics of biogas combustion which is not included in this scope of the study and will be discussed further in the next paper.

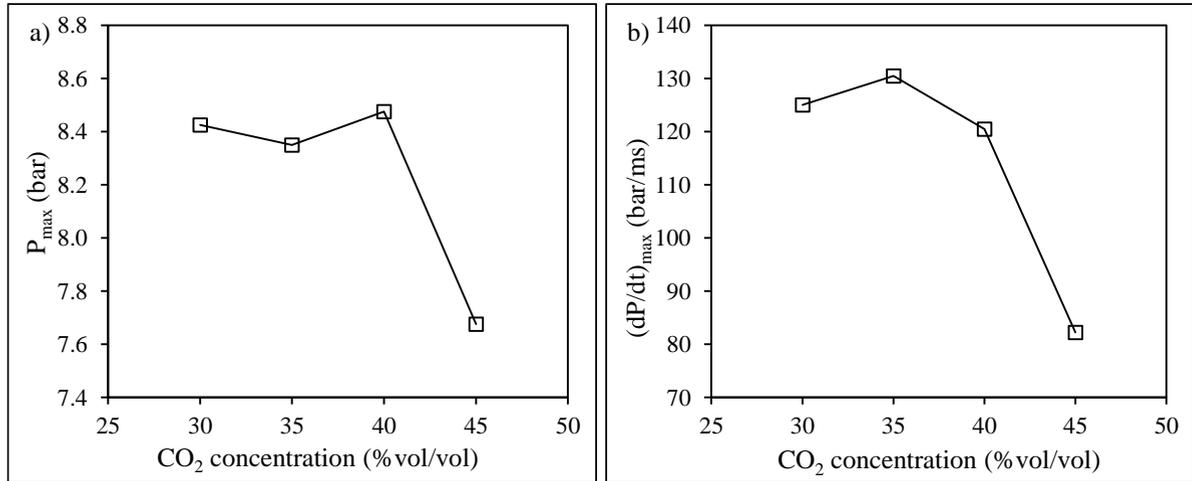


Fig. 3: Biogas/air mixtures at initial ambient temperature and pressure. (a) Effect of CO₂ concentration on the maximum explosion overpressure. (b) Effect of CO₂ concentration on the rate of pressure rise.

Deflagration Index and Flammability Limit of Biogas/Air Mixtures

Gas deflagration index (K_G) is one of the significant factors used to evaluate explosion severity. Eq. 1 was used to calculate K_G in a vessel with a volume other than 1 m³ [19].

$$K_G = \left(\frac{dP}{dt}\right)_{max} \cdot V^{\frac{1}{3}}. \quad (1)$$

Where V is the volume of the vessel (m³) and $(dP/dt)_{max}$ is the rate of pressure rise. Fig. 4 shows the trend of calculated K_G against CO₂ concentration that presence in the biogas. The increase of CO₂ concentration up to 45% vol/vol has reduced the values of K_G . The possible explanation can be based on the nature of CO₂ as a suppression effect. Due to the suppression effect, the presence of CO₂ in biogas may reduce the fuel reactivity, lower the burning rate and hence increase the heat loss to the vessel [20]. This phenomenon reduces the overall mass burning rate that causes the development of the P_{max} and $(dP/dt)_{max}$ decrease and affected the K_G . However, the characteristic is not featured when the concentration of CO₂ in biogas reach 35% vol/vol giving the highest K_G . It was suspected that CH₄ with fast diffusivity properties, has surpassed the CO₂ suppression effect, enhance the overall mass burning rate which causes the P_{max} and $(dP/dt)_{max}$ increase respectively. From the observation, it can be said that biogas with 35 % vol/vol of CO₂ may result in a severe biogas explosion.

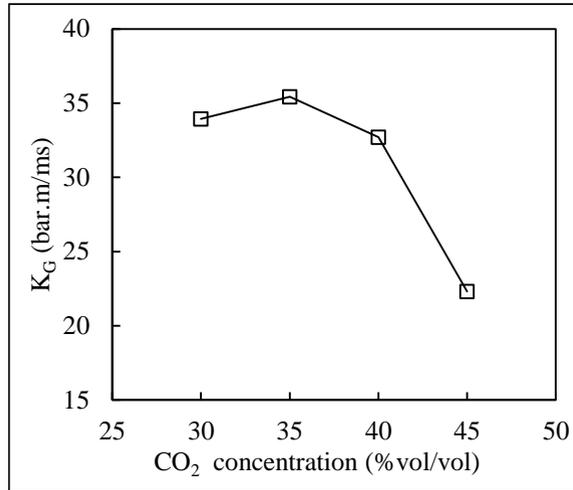


Fig. 4: Biogas/air mixtures at initial ambient temperature and pressure. Effect of CO₂ concentrations on the deflagration index.

Fig. 5 shows the effect of CO₂ on the lower flammability limit (LFL) and upper flammability limit (UFL) of both of the mixtures. In this case study, the flammability limit was calculated using Eq. 2 [21].

$$FL = \frac{100\%}{\frac{y}{L}} \quad (2)$$

Where FL is UFL or LFL (vol%), y is the total combustibles fuel (vol%) and L is the UFL or LFL (vol%). Fig. 5 exhibits the UFL and LFL of biogas/air mixtures. As expected, both LFL and UFL increase as the CO₂ concentration in a biogas increases. The increased flammability limit was caused directly by the suppression effect of CO₂ which improves the biogas flammability limit.

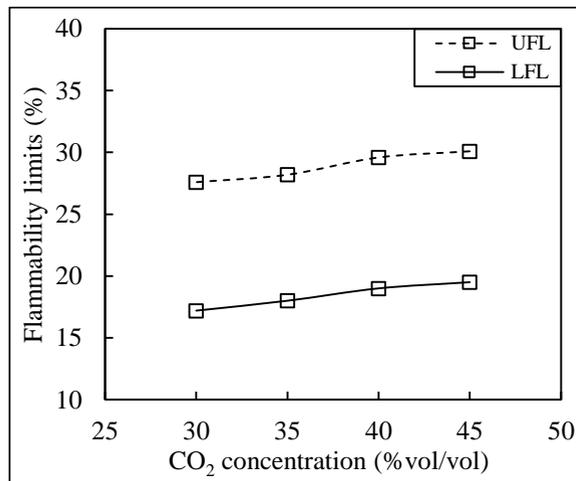


Fig. 5: Biogas/air mixtures at initial ambient temperature and pressure. Effect of CO₂ concentrations on the lower flammability limit and upper flammability limit.

Conclusions

This paper emphasized the effect of equivalence ratio (ER) as well as the presence of CO₂ on explosion severities of biogas (CH₄-CO₂)/ air mixture. The experiments were done in a 20 L spherical vessel over different CO₂ concentrations at initial temperature and pressure. The followings are the conclusion in this study:

- (i) The values of P_{\max} and $(dP/dt)_{\max}$ of biogas/air mixtures were more severe at ER 1.2. Both values of P_{\max} and $(dP/dt)_{\max}$ were found to be 1.8 and 6.7 times respectively, higher than the P_{\max} and $(dP/dt)_{\max}$ at lean concentration. The particular observation was due to the very high specific heat of CH₄ and a fast diffusing reactant, which enhances the overall mass burning rate.
- (ii) The values of P_{\max} and $(dP/dt)_{\max}$ were the least affected at the presence of 45% vol/vol CO₂ content due to the nature of CO₂ which acts as a heat sink in absorbing the heat of combustion. Since CO₂ has a better suppression effect, it reduces the flame temperature that leads to a slower overall mass burning rate and lowered the values of P_{\max} and $(dP/dt)_{\max}$.
- (iii) The K_G of biogas/air mixtures trend was found to be the most severe at 35% vol/vol CO₂ content. Since the K_G was found to be decreasing at higher CO₂ content, it was believed that CH₄ diffusivity properties had surpassed the CO₂ suppression effect which leads to increase in the overall mass burning rate and reflected by the increase in P_{\max} and $(dP/dt)_{\max}$.
- (iv) The effect of the addition of CO₂ to the flammability limit was also significant. As expected from literature, the presence of CO₂ in biogas/air mixture causes the UFL and LFL of biogas to increases. The increase in flammability limits is caused by the suppression effect of CO₂, which improves the biogas flammability limits.

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References

- [1] M. Mitu, V. Giurcan, D. Razus, M. Prodan and D. Oancea, *Journal of Loss Prevention in the Process Industries*, 47 (2017) 110-119.
- [2] L. Dupont and A. Accorsi, *Journal of Hazardous Materials*, 136(3) (2006) 520-525.
- [3] A. Greco, D. Mira and X. Jiang, *Energy Procedia*, 105 (2017) 1058-1062.
- [4] R. Selvaraj, K.T. Abdul Nasir, N.J. Vasa and S.M. Shiva Nagendra, *Sensors and Actuators B: Chemical*, 249 (2017) 378-385.
- [5] R. Lora Grando, A.M. de Souza Antune, F.V. da Fonseca, A. Sánchez, R. Barrena and X. Font, *Renewable and Sustainable Energy Reviews*, 80 (2017) 44-53.
- [6] F.D. Suprianto, *Effect of Carbon Dioxide on Flame Characteristics in Biogas External Premix Combustion*. 2016, Petra Christian University.
- [7] M. Mitu, M. Prodan, V. Giurcan, D. Razus and D. Oancea, *Process Safety and Environmental Protection*, 102 (2016) 513-522.

- [8] A. Di Benedetto, V. Di Sarli, E. Salzano, F. Cammarota and G. Russo, *International Journal of Hydrogen Energy*, 34(16) (2009) 6970-6978.
- [9] L.-K. Tseng, M.A. Ismail and G.M. Faeth, *Combustion and Flame*, 95 (1993) 410-426.
- [10] H.G. Im and J.H. Chen, *Combustion and Flame*, 131(3) (2002) 246-258.
- [11] D. Bradley, M. Lawes and K. Liu, *Combustion and Flame*, 154(1) (2008) 96-108.
- [12] A. Clarke, *Process Safety and Environmental Protection*, 80(3) (2002) 135-140.
- [13] A.S. Huzayyin, H.A. Moneib, M.S. Shehatta and A.M.A. Attia, *Fuel*, 87(1) (2008) 39-57.
- [14] M. Mitu, M. Prodan, V. Giurcan, D. Razus and D. Oancea, *Process Safety and Environmental Protection*, 102 (2016) 513-522.
- [15] W. Qin, F.N. Egolfopoulos and T.T. Tsotsis, *Chemical Engineering Journal*, 82(1) (2001) 157-172.
- [16] Z.R. Wang, L. Ni, X. Liu, J.C. Jiang and R. Wang, *Journal of Loss Prevention in the Process Industries*, 31 (2014) 10-15.
- [17] Y.L. Chan, M.M. Zhu, Z.Z. Zhang, P.F. Liu and D.K. Zhang, *Energy Procedia*, 75 (2015) 3048-3053.
- [18] M.N. Sasongko and W. Wijayanti, *ARPN Journal of Engineering and Applied Sciences*, (2016) 912-916.
- [19] M. Mittal, *Journal of Loss Prevention in the Process Industries*, 46 (2017) 200-208.
- [20] C. Movileanu, D. Razus and D. Oancea, *Fuel*, 111 (2013) 194-200.
- [21] H. Le Chatelier and O. Boudouard, *Bull. Soc. Chim.(Paris)*, 19 (1898) 483-488.