

NUMERICAL STUDY OF CO EMISSION REACTION IN CO₂ DILUTED BIOGAS AND OXY-FUEL PREMIXED COMBUSTION

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Abstract

The conventional biodigester has a high probability of CO₂ contamination. As an inert gas in the combustion process, further investigation needed to clarify the effect of CO₂ in CH₄ premixed combustion. This study aims to determine the effect of CO₂ dilution by using numerical approach to identify the changes in the chemical reaction chain especially in CO gas formation. To get the most suitable mixture, the range of equivalence ratio was varied from 0.11-3.14 and 0.5-1.68 in CH₄/CO₂/O₂ and CH₄/CO₂/Air respectively. The amount of CO₂ diluted in each reactant mixture was varied from 0-40% mass based on conventional biogas composition. The flow rate was maintained in ±6 L/min. The distance of the two counterflow nozzles was 20mm so that the stagnation point gained at 10mm in z coordinate. Results from this study showed a decreasing temperature caused by CO₂ addition that more significant on the fuel-rich side. CO₂ does not only decrease the temperature by absorbing heat but also has the potential to make changes in chemical reactions path. On both reactants, the CO mass fraction showed an increasing value as the CO₂ was added to the mixture. This is due to the decreasing heat release rate of some reactions that convert CO into CO₂. Those reactions such as $\text{CO} + \text{O} (+\text{M}) \leftrightarrow \text{CO}_2 (+\text{M})$, $\text{CO} + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{O}$ and $\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$ reactions.

Keywords: Biogas, CO Reaction, Counterflow, Premixed.

1. Introduction

Combustion is one of the most widely used energy conversion. The high amount of energy generated in such a short time makes combustion technology would still be existed for around 40 years from now on. Biogas that produced from conventional reactors has a debility due to its high amount of CO₂ (0-40%) [1]. Thus, it could lead in decreasing combustion performance of biogas.

Some previous researches have been held to analyse the effect of CO₂ in CH₄ combustion. The existence of CO₂ could change the flame speed in a leaner AFR mixture [2]. Experimental research using a Bunsen burner showed a decreasing flame speed along with the higher amount of CO₂ diluted in each mixture. The risk of flame extinction due to the blow-off phenomenon also tend to increase. It also has some effects on the fuel consumption rate [3]. Along with the slower flame speed, the risk of explosion in a reservoir decreased [4]. A reduced temperature also gained in CH₄/CO₂/O₂ counterflow premixed combustion along with the higher amount of CO₂ in the mixture [5].

The lower temperature generated in a combustion process could lead to a reduction of NO_x production. Besides that, the higher amount of CO₂ could potentially increase the amount of CO produced. High CO emissions generally lead to poor combustion efficiency. This is due to the higher fuel needed to produce the same amount of energy [5]. In a counterflow diffusion flame investigation, the higher CO₂ dilution showed an extended yellow flame-coloured region. It could be determined as a higher amount of unburnt fuel that occurred. Therefore, the flame stabilities were also more dependent on the diffusion rate between fuel and oxidation [6].

From the background explained above, it is needed to make a further investigation, especially to reduce the negative effects of CO₂ on premixed biogas combustion. The focus of the previous studies generally was making CO₂ as a replacement of N₂ in oxidation mixtures. In this research, N₂ was still considered as an air mixture, while the CO₂ was added simultaneously in the fuel side mixture. By using the 1-dimensional approach in counterflow configuration, it is expected to get the most effective proportion of mixture and its product species formation.

2. Research Methods

This study conducted using the 1-dimensional numerical approach in a premixed counterflow burner. There were two kinds of mixture studied. CH₄ / CO₂ / air represents biogas combustion in an air environment. The air composition used an O₂: N₂ ratio of 1:3.76 in all variations. The second mixture compounded of CH₄ / CO₂ / O₂ represents oxy-fuel combustion of biogas. The equivalence ratio was varied in all range of flammability limits. It was 5% - 15% fuel volume fraction in the air environment and 5% - 61% fuel volume fraction in O₂ environment [7]. It was thus resulting in an equivalence ratio of 0.5 - 1.68 and 0.11 - 3.14 in air and O₂ environment respectively. The amount of CO₂ added was varied 0%-40% of total reactant mass in each equivalence ratio variations. Some combustion parameters that investigated in this study was the peak temperature and CO mass fraction in the product side.

Some parameters that held constant in every test were: the counterflow pipe diameter used was 2.45 cm. Inlet reactants temperature and the pressure was 300 K and 1 atm. The volumetric flow rate of reactants was ± 6 L / min. The distance

between two opposed nozzle pipe was 20 mm; in that case, the stagnation point was at 10 mm of z coordinate. All these physical values were taken to be the same as the previous experimental study [8].

The calculation was held using CANTERA 2.2.0 counterflow premixed flame code along with the GRI-Mech 3.0 as the reaction mechanism database. The programming language used to run the Cantera's code was Python 3.4 along with NumPy as numerical package codes. GRI-Mech 3.0 was chosen for chemically kinetic calculation. It was consisted of 325 chemical reactions data with 53 species that also provide the reaction rate and thermodynamic properties data. Those data were based on many types of research held by Technion NASA that optimized for methane combustion [9].

Research Installation

As could be seen in Fig. 1, The reactants that consisted of fuel and oxidizer flowed from two opposed nozzles identically. The combustion process will produce two identical flattened flames on both sides. Because of those two-flow similarity and the flat flame geometry, a one-dimensional analysis could be held on this case [10].

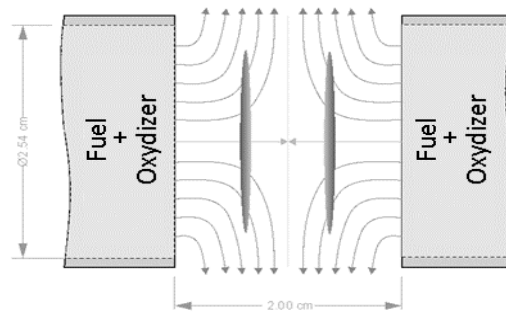


Fig. 1. Scheme of counterflow premixed combustion installation.

Counterflow Premixed Flame class was used in this study. This class was based on One Dim class which contain the basic equation code for 1-dimensional analysis domain. The calculation was written based on the axisymmetric flow field with a stagnation plane in to solve this problem is as follow [7].

- Axial momentum balance

$$\frac{\partial p}{\partial z} = -4 \frac{d}{dz} \left(\frac{U}{\rho} \right) + \frac{4}{3} \frac{d}{dz} \left[2\mu \frac{d}{dz} \left(\frac{U}{\rho} \right) + \frac{\mu}{\rho} \frac{dU}{dz} \right] - 2\mu \frac{d}{dz} \left(\frac{1}{\rho} \frac{dU}{dz} \right) \quad (1)$$

- -Radial momentum balance

$$\frac{1}{r} \frac{\partial p}{\partial r} = 2U \frac{d}{dz} \left(\frac{1}{\rho} \frac{dU}{dz} \right) - \frac{1}{\rho} \left(\frac{dU}{dz} \right)^2 + \rho \left(\frac{w}{r} \right)^2 - \frac{d}{dz} \left[\mu \frac{d}{dz} \frac{\mu}{\rho} \frac{dU}{dz} \left(\frac{1}{\rho} \frac{dU}{dz} \right) \right] \quad (2)$$

- -Energy conservation

$$\rho u c_p \frac{dT}{dz} = \frac{d}{dz} \left(\lambda \frac{dT}{dz} \right) - \sum_{k=1}^K \rho Y_k V_k c_{pk} \frac{dT}{dz} - \sum_{k=1}^K h_k W_k \dot{\omega}_k \quad (3)$$

- -Species conservation

$$\rho u \frac{dY_k}{dz} = - \frac{d}{dz} (\rho Y_k V_k) + W_k \dot{\omega}_k \quad (4)$$

The boundary conditions of this simulation were the axial velocity (u), radial velocity (v), temperature (T), lambda $1 / r \partial p / \partial r$ (A) and the mass fraction of species (Y_k) is not influenced by the radial coordinate. The calculation was performed on a small Mach number whereas $dP / dz = 0$, and in that case, the value of lambda (A) is constant ($1 / r \partial p / \partial r = \text{constant}$).

To solve these equations, Cantera used Newton's iteration methods. The settlement is done in two stages. The first stage is to solve the equation without energy enabled at every point of z coordinate that has been determined. This stage resulted in a rough starting approximation of the solution. The second stage is a process of recalculation at all starting point that then being refined simultaneously to get a smoother solution.

3. Results and Discussion

3.1. CH₄/CO₂/ air reactants

Based on Fig. 2, The maximum temperature data (peak temperature) showed a trend quite like the adiabatic temperature. That is the highest temperature is at an equivalent ratio of close to 1, and the temperature rich fuel mixture was higher than leaner fuel mixture. The highest maximum temperature gained was 2234.1 K at a ratio of 1.03 with the amount of CO₂ 0%. At the same time, the lowest peak temperature was 1455.9 K obtained in an equivalent ratio of 0.5 with the addition of 40% CO₂. The presence of the heat transferred along with the z coordinates affects the amount of calorific value that can be absorbed by the species to raise its temperature—besides the mass transfer flow stagnation on the analysis of 1D, causing the presence of the effects of differences in flow rate at any point in the z coordinate (strain rate) which also affects the temperature generated by the combustion.

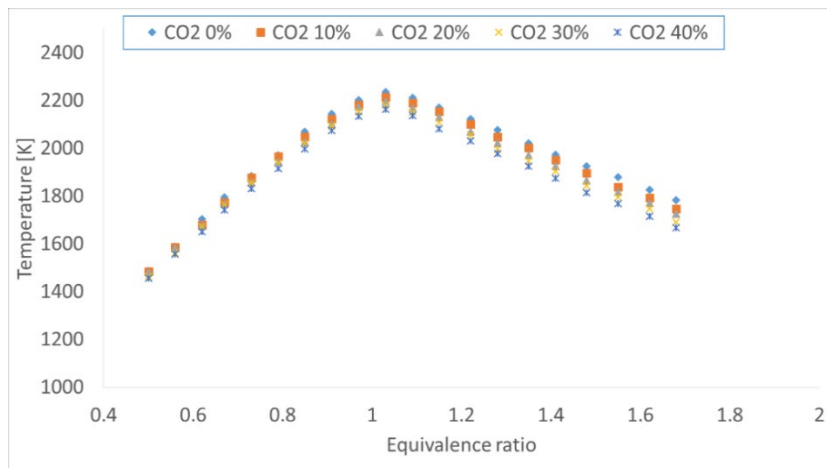


Fig. 2. The peak temperature of CH₄/CO₂/air in each equivalence ratio.

Gas emissions analysis

CO species is a result of incomplete combustion of due to insufficient availability of O₂ species in the reactant mixture.

Shown in Fig. 3, CO mass fraction tend to form more in line with the magnitude of the equivalent ratio. CO species begin to rise at an equivalent ratio of 0.85 with the amount of 0.1%. The highest CO mass fraction gained at an equivalent ratio of 1.68 and CO₂ 40% with the value of 11.4%. The effect of adding more CO₂ could be seen started at an equivalence ratio of 1.15 - 1.68. At those range of equivalence ratio, the mass fraction of CO tends to increase along with a greater amount of CO₂ added. CO₂ addition had the greatest effect at an equivalent ratio of 1.68, which determined by its largest decline in CO mass fraction about 1.4%. Theoretically, when it reaches an equivalent ratio of 1, the overall species of CH₄ and O₂ should be burned out completely to become a species of CO₂ and H₂O. However, the combustion temperatures were high enough to make the species of O₂ react to form NO_x, albeit in relatively small amounts as in Fig. 4. It causes a small part of the species CH₄ could not burn completely which then resulting in a 1% mass fraction of species CO.

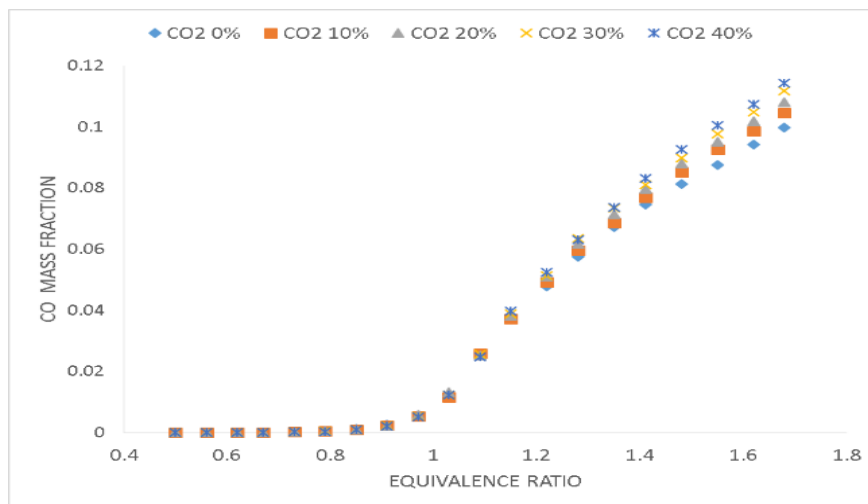
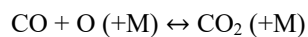
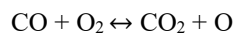
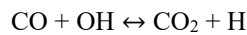
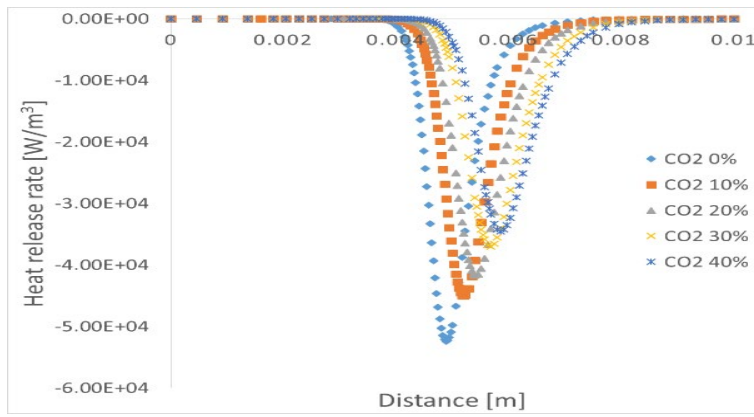


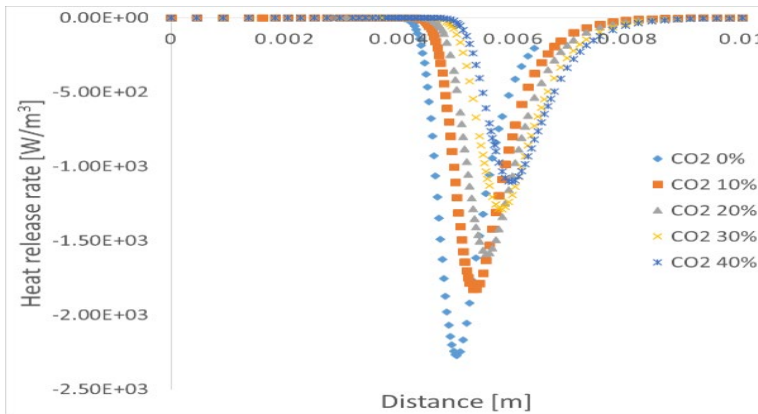
Fig. 3. CO mass fraction in each equivalence ratio.

On the leaner fuel mixture, no CO species formed because the entire CH₄ species completely burned out where the oxidizer conditions are abundant. On the rich fuel mixture, the lack of O₂ to oxidize the fuel causes species CO tend to be raise because of incomplete combustion. The addition of CO₂ in every equivalence ratio could increase the amount of the formation of CO species. In overall hydrocarbon fuel combustion, CO species acts as an intermediate species before the formation of CO₂. The process of oxidation of CO to CO₂ species takes place at the final stage of combustion. In most cases of arson, the most dominant reaction for species of CO to CO₂ are those three following reactions.

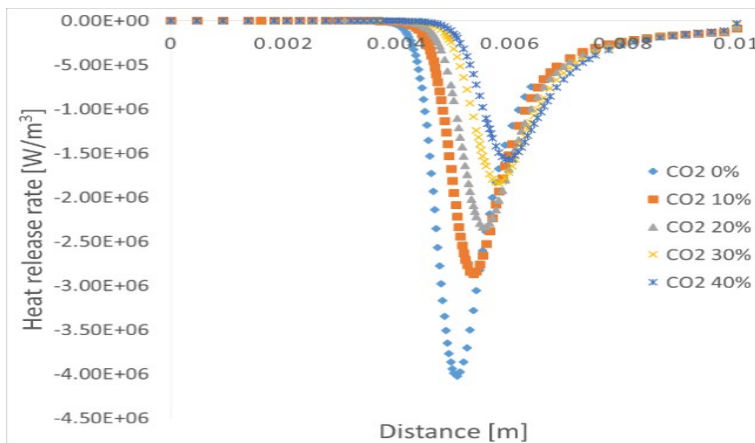




(a) $\text{CO} + \text{O} (+\text{M}) \leftrightarrow \text{CO}_2 (+\text{M})$.



(b) $\text{CO} + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{O}$.



(c) $\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$.

Fig. 4. Heat release rate of some reaction that convert CO into CO₂ at the equivalence ratio of 1.68 in each point.

Figure 4 can be observed that the three reactions studied there had a drop-in heat release rate at any additional CO₂. The highest heat release rate of CO + O (+M) ↔ CO₂ (+M) reaction worth -52408 W / m³ without the addition of CO₂ and harshly down into -34525 W / m³ in the addition of 40% CO₂. Reaction CO + O₂ ↔ CO₂ + O, had the highest heat release rate that worth -2275 W / m³ without the addition of CO₂ and then fell to -1104 W / m³ in the addition of 40% CO₂. While the reaction of CO + O₂ ↔ CO₂ + O had the highest heat release rate value at the peak was -4024993.6 W / m³ without the addition of CO₂ and harshly fell to -1573279.7 W / m³ with the addition of 40% CO₂. One of the required conditions for CO + OH ↔ CO₂ + H to react is the availability of species OH. OH species was largely formed through previous chain branching reactions which experimentally unable to react at temperatures below 1100 K. The reaction CO + CO₂ + O₂ ↔ O and CO + O (+M) ↔ CO₂ (+M) can only react on temperatures above 1100 K. in addition to both reactions require the availability of sufficient O₂ to react. So that the fuel-rich conditions made the reaction CO + CO₂ + O₂ ↔ O and CO + O (+M) ↔ CO₂ (+M) difficult to react. Due to the decrease in temperature in each of CO₂ added, the availability of OH to sustain the reaction CO + OH ↔ CO₂ + H will be fewer [6]. So, with fewer of those three reactions to react would result in an increase in the formation of CO mass fraction with the addition of CO₂.

Another combustion product's species that had a sufficiently high mass fraction value in this research was the H₂ species. These species arise because of incomplete combustion of CH₄ species. H₂ species is a combustible gas so that the exhaust gas product (H₂ and CO) could be used through a recycled combustion application.

As could be seen in Fig. 5, H₂ species begin to form at the equivalent ratio of 0.97 the value of mass fraction around 0.2%. H₂ mass fraction raises higher when the equivalent ratio is greater. The highest mass fraction values are at an equivalent ratio of 1.68 without CO₂, with a value of 10.68%. Unlike the CO species, the effect of adding CO₂ to the formation of species H₂ had a negative effect. There was a decrease in the mass fraction of H₂ in line with the addition of CO₂. The most significant effect of adding CO₂ occurred at an equivalence ratio of 1.68 with the difference between of mass fraction about 2.3% without and with the addition of CO₂.

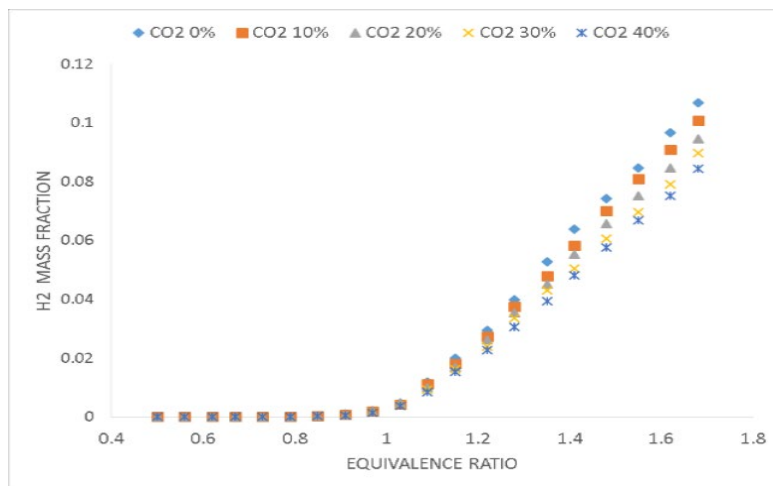
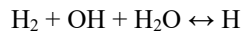


Fig. 5. H₂ mass fraction in each equivalence ratio.

The reaction which could convert H₂ species to become H₂O is the following reaction.



This reaction is reversible so that it can take place in the reverse condition. If it was observed on each z coordinates, it could show that the formation of H₂ still occurred along with the point behind the flame front. Figure 6 shows the development of the mass fraction of species H₂ and H₂O on the variation ratio of 1.68 in overall CO₂ additions. The location of the flame can be represented by the area where the species begin to form H₂O (the reaction zone). Along with the addition of CO₂ location further away from the flame end of the pipe nozzle (z = 0). This indicates a decrease in velocity of the fire along with the addition of CO₂ where flame propagation velocity is directly proportional to the temperature produced by combustion.

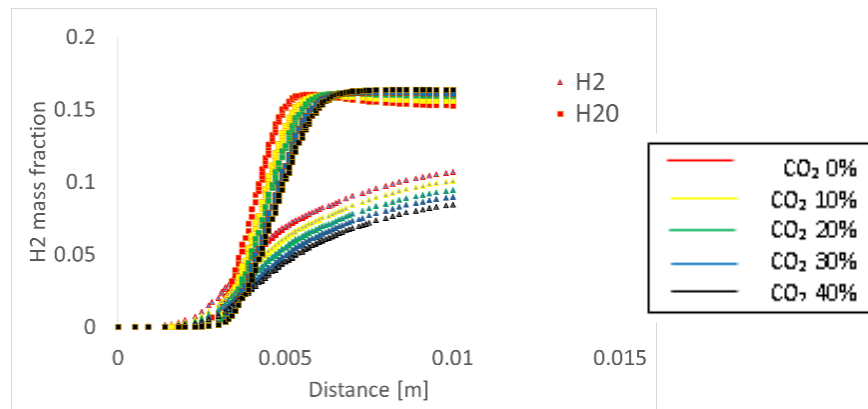


Fig. 6. H₂ mass fraction at an equivalence ratio of 1.68 along the z-axis.

Figure 6 indicates that the formation of H₂ was not only presented in the reaction zone. H₂ formation also occurs in the zone after the flame front. The interesting thing is there was an increase in the mass fraction of H₂ that was also accompanied by a decrease in mass fraction H₂O. The increase in the mass fraction of H₂ was highest in CO₂ 0% addition. H₂O mass fraction reached the peak value at 0.0057 m with a value of 16:04%. Then the decline began at 0.0059 m till it reached 0.001 m with the value of 15:28%.

It appears that there was a dissociation of H₂O to back become H₂. The H₂O dissociation reaction species into species H₂ mainly caused by an H₂ + OH + H₂O ↔ H reaction that occurred in the reversed path.

3.2. CH₄ / CO₂ / O₂ reactants

As could be seen in Fig. 7, the value of the highest peak temperature was gained in the equivalence ratio of 1.06 without CO₂ addition. While the value of the lowest peak temperature gained in equivalence ratio of 3.14 with the addition of CO₂ 40%. It was shown that the temperature goes lower in every addition of CO₂ at the same equivalence ratio. At equivalence ratio of 0.11 the peak temperature ranges from 1444.5 - 1413.8 K. Whereas in an equivalent ratio of 3:14 is worth 1811 K and 1693 K on the addition

of CO₂ 0% and 10%, then drastically down to the value of 1279 K, 1220.3 K and 1177.6 K upon addition of CO₂ 30 %, 40% and 50%. This phenomenon is caused by O₂ levels were getting closer to upper flammability limit range.

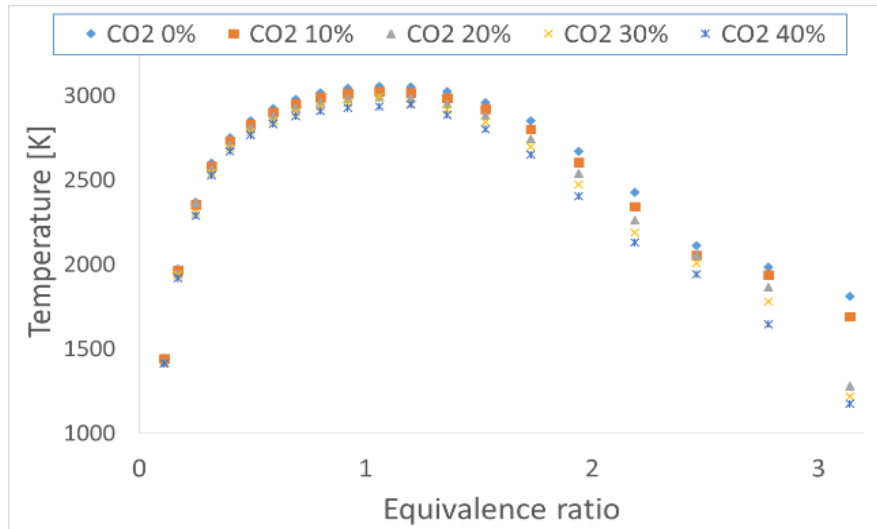


Fig. 7. The peak temperature of CH₄/CO₂/O₂ in every equivalence ratio.

Molecularly the CO₂ species has a Lennard-Jones collision diameter that sufficiently larger (3760 Angstrom) [11] if compared to O₂ species (only has a diameter of 3,460 Angstrom). This makes the possibility of CH₄ to be able to collide with O₂ getting smaller. The addition of CO₂ resulted a lower temperature at same equivalence ratio. The mean difference of temperature decrease on each additional CO₂ can be seen in Fig. 7.

It is seen that the temperature difference was in line with increasing equivalent ratio. The highest mean difference between the peak temperatures is worth 158.35 K at equivalence ratio of 3.14 and the lowest worth 7.67 K at equivalent ratio of 0.11. It had the same tendency with CH₄/CO₂/air data, both showing the impact of adding more CO₂ was more significant on the fuel-rich mixture.

Gas emission analysis

Figure 8 showed that the formation of CO species getting higher along with the increase of equivalent ratio. CO species begins to form at an equivalence ratio of 0.32. These phenomena were not consistent with the hypothesis in which the CO species should be formed in the equivalent ratio greater than 1. If it were observed from installation scheme and the input parameters used in this study, the large inlet pipe nozzle 2.45 cm in diameter and low flow rate of the reactants 6 L / min caused the flame propagation velocity were faster than the speed of the reactants. The flames were so thin makes CH₄ species did not have enough time to convert CO into CO₂ species. This could be seen from the CH₄/CO₂/O₂ flame was located very close from the inlet nozzle.

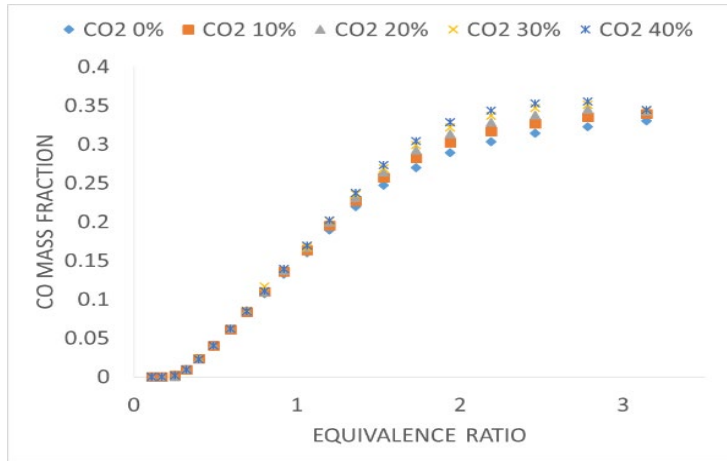
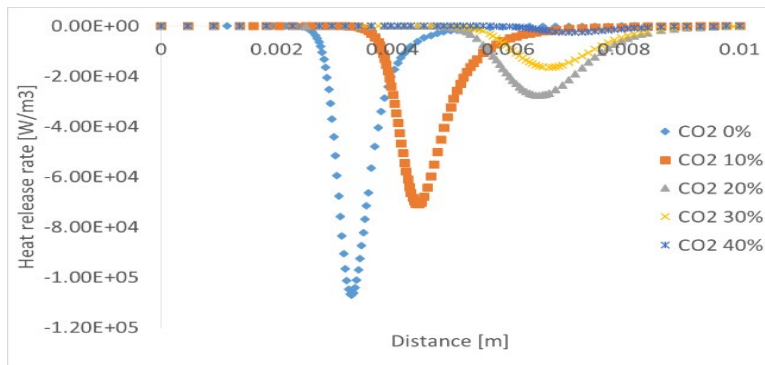


Fig. 8. CO mass fraction in each equivalence ratio.

The effect of adding CO₂ could lead to further higher the formation of CO species. The highest CO mass fraction of species gained at the equivalent ratio of 2.78 with the addition of 40% CO₂. The additions of CO₂ could reduce the temperature that made the possibility of the reaction which convert CO into CO₂ species occurred are getting smaller.

Figure 9 show the three reactions that observed showed that there was a decrease in heat release rate along with the addition of CO₂. Figure 9(a) shows that the reaction of CO + O (+ M) ↔ CO₂ (+ M) occurred further away from the inlet nozzle tip along with the increasing CO₂. This indicated the presence of CO₂ decreased the flame propagation speed of the mixture. The existence of the reaction CO + OH ↔ CO₂ + H began to disappear in the addition of more than 30% CO₂. Reaction CO + OH ↔ CO₂ + H suffered the highest loss effects on any additional CO₂ when compared with the two other reactions. This is mainly due to the availability of OH was getting a bit lower with the addition of CO₂ especially in formation reaction of OH which happened before those reactions. A decrease in the existence of three of these reactions made the CO species that have formed could not be converted into CO₂. So that by the decline in the existence of these reaction makes the species CO left until the final stages of combustion excessively.



(a) CO + O (+M) ↔ CO₂ (+M)

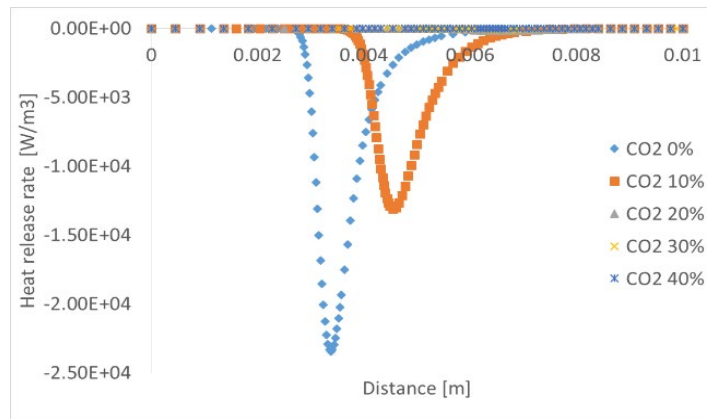
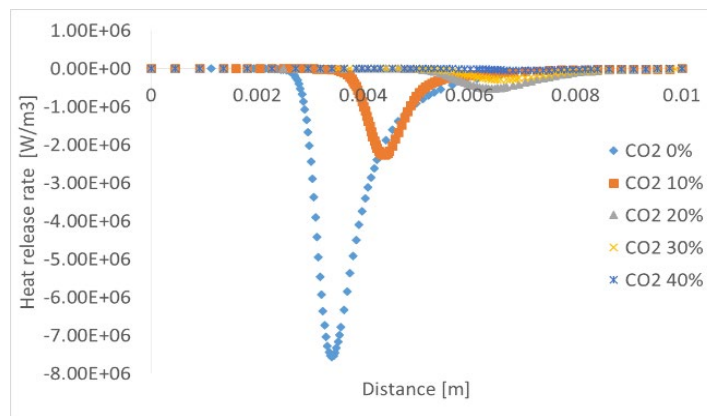
(b) $\text{CO} + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{O}$ (c) $\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$

Fig. 9. The heat release rate of some reaction that converts CO into CO₂ at the equivalence ratio of 1.68 in each point.

The experimental data showed an interesting phenomenon in which the equivalent ratio approaching 1 with a flow rate of the reactants 6 L / min occurs a second flame front that moving toward the inlet nozzle in Fig. 10 could be seen some of the visual data combustion in some equivalent ratio.



Fig. 10. Experimentally flame front visual data of CH₄/CO₂/O₂ with equivalence ratio of 0.90 and flow rate at 6 L/min

When compared with the data from this simulation, it could be determined that the upper flame was the remaining of unburned fuel in the form of H₂ and CO which burned down after the primary flame. The primary flame moved downward as the

equivalent ratio closer to 1. The reactants were burned very quickly in the primary flame thus make the most of the slow reaction such as CO → CO₂ cannot take place optimally. As a result, more and more species of unburned fuel on the fire lit in the second flame. If the flame propagation speed is too fast, it could lead to a higher risk to explosion. The presence of CO₂ in the biogas can reduce the flame speed. But the equivalent ratio conditions in the mixture composition have the most significant role in the flame propagation velocity value

4. Conclusion

Results from this study showed a decreasing temperature caused by CO₂ addition that more significant on fuel rich side. CO₂ does not only decrease the temperature by absorbing heat, but also has a potential to make changes in its chemical reactions path.

Based on the numerical analysis, CH₄/CO₂/O₂ mixture tends to produce higher CO than CH₄/CO₂/air. CO emission occurs on a higher equivalence ratio on both reactants where the supply of O₂ gas is abundant.

On CH₄/CO₂/O₂ and CH₄/CO₂/air mixture, the CO emission mass fraction showed an increasing value as the CO₂ were added to the mixture. This is due to the decreasing heat release rate of some reactions that converts CO into CO₂. Those reactions such as CO + O (+M) ↔ CO₂ (+M), CO + O₂ ↔ CO₂ + O and CO + OH ↔ CO₂ + H reactions.

Nomenclatures

r	Radial coordinate, m
T	Temperature, °K
U	Velocity function in axisymmetric, kg/m ² .s
u	Axial velocity, m/s
v	Radial velocity, m/s
w	Circumferential velocity, m/s
Y_k	Mass fraction of k -th species
z	Axial coordinate, m

Greek Symbols

λ	Thermal conductivity, W/m ² °K
Ψ	Flow function, kg/m.s
μ	Dynamic viscosity, kg/m.s
ρ	Mass density, kg/m ³

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