NUMERICAL ANALYSIS OF NO_x FORMATION IN CO₂ DILUTED BIOGAS PREMIXED COMBUSTION

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Abstract

A further investigation of premixed biogas combustion towards the NO_x formation is presented in this study. The purpose of the simulation is to determine the addition of CO₂ in biogas fuel to the combustion behavior of premixed biogas on NO_x formation, and to determine the occurrence of NO_x in the pre-mixed biogas combustion. In this study, the Counterflow Premixed Flame class is used where this class is based on the One Dim class which is the basis for simulations with a 1-dimensional domain. The Counterflow Premixed Flame class uses an axisymmetric stagnation flow domain which has been written based on the equations. Cantera uses Newton's method to solve them. Completion is carried out in two stages. The first stage is to solve the solution using the equilibrium at each *z* coordinate point that has been determined. Many estimation starting points are determined from the start of the program. The second stage is the recalculation process at each point and then subdivided to get a smoother solution. The pre-mixed excess CO₂ biogas fuel and air combustion analyzed using a 1-dimensional numerical study. The diluted CO₂ mass fraction ranged between 0–40 %. The CH₄/CO₂/air volume flow rate was maintained in $\pm$ L/min. The analysis implements the 1-D Counter Flow approach. Two counterflow nozzles were 20mm in diameter and the flame stagnation point at 10 mm. The results show that NO_x mass fraction formed only on a fuel-lean mixture of CH₄/CO₂/air and its values decreased along with CO₂ added. The addition of CO₂ could reduce the NO species mass fraction down to 18 %, and NO₂ reduction down to 7 %. This is mainly caused by a decreasing heat release rate of NO+N $\leftrightarrow$ N₂+O, N+O₂ $\leftrightarrow$ NO+O, N+OH $\leftrightarrow$ NO+H, and N+CO₂ $\leftrightarrow$ NO+CO reactions. The N+CO₂ $\leftrightarrow$ NO+CO reaction increased as CO₂ was added but its values were not as much as the decline of three other reactions.

Keywords: numerical study, NO_x formation, diluted CO₂, premixed biogas combustion, counterflow.

DOI: 10.21303/2461-4262.2021.002072

1. Introduction

Human consumptive behavior towards energy use has increased in recent decades. This is motivated by technological developments and of course an increase in the number of human populations, however, the large level of energy consumption is not matched by the amount of supply of energy sources that will eventually run out. Therefore an alternative energy source is needed as a substitute for non-renewable energy sources [1–3].

One of the alternative energy sources currently being developed is biogas [2]. Biogas is defined as a gas released by organic materials (such as livestock manure, human dung, straw, husks, and leaves of sorted vegetables) which are fermented or undergo a methanation process [4]. Biogas is a gas mixture produced by methanogenic bacteria that occurs in materials that can decompose naturally under anaerobic conditions [5, 6].

Biogas is a gas produced by anaerobic activity or fermentation of organic materials which can be degraded naturally. Materials for making biogas can be found easily in the environment around us. Organic waste is the main material for making biogas. Substrates containing high lignin, cellulose, and hemicellulose require special handling before the anaerobic digestion process. So that from the formation of biogas et two benefits at the same time, namely obtaining biogas as fuel and reducing the volume of waste optimally [4, 7].

The composition of the gas produced by the formation of biogas varies depending on the source of the material used. The amount of methane gas content in the anaerobic digestion process

is one of the important criteria as a benchmark for selecting the main material for making biogas. The higher the content of methane gas formed from the anaerobic digestion process, the better the potential for biogas to be used as fuel [8, 9].

The content of biogas itself includes CH_4 (50 %–70 %), CO_2 (30 %–40 %), H_2S (0 %–10 %), H_2O (0.3 %), N_2 (1 %–2 %), H_2 (5 %–10 %) and other gases [10]. The component that has the potential as fuel is CH_4 because the calorific value contained in it is quite large. The largest content in biogas after CH_4 is CO_2 [11]. The existence of CO_2 itself is a detrimental thing. This is due to its characteristics which can reduce the calorific value contained in the biogas. The high specific heating value of CO_2 gas will make some of the heat from combustion absorbed by CO_2 gas. The dissolved CO_2 content in the fuel will decrease the rate of the combustion reaction which results in the biogas combustion process requiring a longer time [12].

Counterflow burner installation is an installation that is very suitable for studying combustion characteristics. This is because this installation produces a simple flame in which the flame front and the shadow area of the flame are visible [13]. Counterflow burners use two flows in a pipe in opposite directions. If the two flows have the same flow rate, it will form an almost flat flame [14].

Numerical simulation is one solution to solve the combustion problem. With the increasing number of previous experimental studies that can be used as a reference, making today's numerical simulations more robust and the results of the calculations more accurate. The development of technology in the field of computerization also makes numerical simulation-based research easier. In general, numerical simulation can provide analysis results that can be considered in a relatively fast time and at a much more affordable cost when compared to experimental based research.

2. Materials and methods

The anaerobic process in conventional biogas reactor produces CO_2 gas which affects the biogas combustion characteristic. This study aims to investigate the CO_2 roles in NO_x production of conventional biogas especially in premixed combustion. In order to analyze the combustion characteristic, this study focusing in the chemical reaction chain that contribute to NO_x formation. Thus, the 1D analysis in counterflow reacting flow are used in this study. The study focuses in the detailed investigation based on the flame characteristic especially in chemical reaction analysis. However, this study only limited to a steady 1dimensional analysis.

The 1D analysis is only performed on one side of the opposite flow. There are two coordinates, namely the r (radial) coordinate and the z (axial) coordinate. Where the time of the calculation engineering was carried out so that all the existing parameters were only affected by the z coordinate. Each calculation will produce the values of combustion parameters such as species mass fraction (x), temperature, axial velocity (u), and radial velocity (v). These parameters are calculated at each node along the z coordinate direction flow path (starting from the nozzle to the point of stagnation). The number of nodes in each calculation varies depending on the number of reactions that occur from the mixture provided.

Before doing numerical calculations using Cantera 2.2.1, several calculations are required. The gas specifications used in the calculation is from the GRI-Mech 3.0 database. By using pre-determined conditions, namely a pressure of 1 atm and inlet temperature of 300 °K, gas specifications are shown in **Table 1**.

Table 1
Gas Specification

Species	Density [kg/m ³]	Entalphy [J]	U [J]	Entropy [J/K]	C_p [J/Kmol °K]	C_v [J/Kmol °K]
CH_4	0.652	-7.45×10^7	-7.703×10^7	1.866×10^5	3.576×10^4	2.745×10^4
O_2	1.299	5.436×10^4	2.440×10^7	2.053×10^5	2.939×10^4	2.107×10^4
CO_2	1.666	-3.934×10^8	-3.959×10^8	2.140×10^5	3.722×10^4	2.890×10^4
N_2	1.138	5.522×10^4	-2.439×10^7	1.917×10^5	2.908×10^4	2.076×10^4

In this study, the CounterflowPremixedFlame class is used where this class is based on the OneDim class which is the basis for simulations with a 1-Dimensional domain. The CounterflowPremixedFlame class uses an axisymmetric stagnation flow domain which has been written based on the equations.

Fig. 1. 1-Dimensional premixed flame nodes

Cantera uses Newton's method to solve them. Completion is carried out in two stages. The first stage is to solve the solution using the equilibrium at each z coordinate point that has been determined. Many estimation starting points are determined from the start of the program. The second stage is the recalculation process at each point and then subdivided to get a smoother solution.

The data collection process is carried out in several stages.

To simulate the combustion of a counterflow premixed flame in all variations, the following steps are carried out:

- a) the process of making 1 main line of coding for the counterflow premixed flame simulation. The coding master file is saved in .py form to be operated in the IDLE Python 3.4.3 window;
- b) calculation of input data for the entire specified variation;
- c) in various types of reactants $\text{CH}_4/\text{CO}_2/\text{air}$. Specified oxidation;
- d) determined x_{CO_2} ;
- e) enter the parameters of reactant composition, mass flux, and combustion conditions according to the calculation data (b) into the variables that have been prepared;
- f) enter the numerical calculation criteria parameter i.e.:
 - relative tolerance for steady conditions = 1.0×10^{-7} ;
 - absolute tolerance of steady-state = 1.0×10^{-13} ;
 - relative tolerance of the stepping process time = 1.0×10^{-7} ;
 - absolute tolerance of time stepping process = 1.0×10^{-11} ;
 - ratio = 3, slope = 0.1, curve = 0.2 and prune = 0.02;
- g) enter the name of the .csv file to be used as the container for the calculation results;
- h) the process of running the program in the Python Shell window. If there is convergence in the iteration process, the procedure (g) is repeated by changing the absolute tolerance value and the relatively steady-state = 1.0×10^{-20} . If there is still an error, then a round of 3 digits behind the comma is carried out on the mass flux value in and out of the flow stage (f). If there are no errors, the procedure continues to step (k);
- i) the calculation operation was successful, the calculation result data has been saved in the step (h) .csv file. The output in the Python Shell window is stored in a .txt file with the same file name as the .csv file;
- j) steps (f)–(k) were repeated for variations of x_{CO_2} 10 %, 20 %, 30 % and 40 %;
- k) steps (e)–(k) are repeated for another variation of $x_{\text{Oxidators}}$;
- l) steps (d)–(m) are repeated for various types of $\text{CH}_4/\text{CO}_2/\text{O}_2$ reactants;
- m) the data obtained from each program run are sorted based on the data from the dependent variable that is sought and graphed for further analysis.

Formulation of the problem:

1. How is the effect of adding CO₂ to biogas fuel on the combustion behavior of pre-mixed biogas on NO_x formation?
2. How does NO_x occur in pre-mixed biogas combustion?

3. Results and discussion

Fig. 2 shown that the temperature decrease caused by the addition of CO₂ is greater at the equivalent ratio > 1. This means that the effect of CO₂ is more significant on combustion with a rich fuel mixture. The smallest temperature difference is 10,698 °K is obtained at the equivalent ratio of 0.5, while the largest difference is 28.64°K is obtained at the equivalent ratio of 1.68.

Fig. 2. The temperature difference in each of equivalence ratio

It can be seen that the temperature decrease caused by the addition of CO₂ is greater at the equivalent ratio > 1. This means that the effect of CO₂ is more significant on combustion with a rich fuel mixture.

In fuel-lean mixture combustion, the effect of adding CO₂ is not too significant due to the abundance of oxidizing species in the reactant mixture. When observed from a collision theory point of view, this makes the possibility of CH₄ molecules to collide with O₂ very large. So that the role of CO₂ as a diluent that inhibits or reduces the number of successful collisions between CH₄ and O₂ is not too large. As the number of oxidizers decreases at a greater equivalent ratio, the presence of CO₂ on the reactant side can reduce the number of collisions. With the presence of N₂ species in the CH₄/CO₂/air reactant, the possible number of collisions between CH₄ and O₂.

CO₂ influence towards the formation of harmful species NO_x (NO₂ and NO) has been reviewed on the overall equivalent ratio variations. The data taken was the peak mass fraction of species of NO and NO₂ along with z coordinates. The results can be seen in **Fig. 3**.

Fig. 3. NO mass fraction in each equivalence ratio

NO species can be formed when combustion reached high temperature and the unburned O species for pairs are presented. As shown in **Fig. 2**, the highest mass fraction of NO species was $3,059 \times 10^{-3}$ gained at 0.85 equivalent ratio variations with the additions of CO₂ 0 %. In rich-fuel mixture regions, there is no species formation of NO presented. This is due to the lack of O species supply.

The O_2 species was completely reacted with the fuel species at nearly the stoichiometric. The decline of NO mass fraction in the lean fuel mixture was because of some reaction that converts NO into species NO_2 . This can be seen in **Fig. 3** that on each additional CO_2 impairment the largest decrement of NO mass fraction occurred at an equivalent ratio of 0.85. A further analysis was conducted at this equivalence ratio by analyzing the heat release rate of some reaction that produces NO species.

Fig. 4, a shows the heat release rate from the reaction of $NO+N \leftrightarrow N_2+O$ at each of the z coordinates. It is seen that the reaction $NO+N+O \leftrightarrow N_2$ has the largest heat release rate of 2026.3 W/m^3 with the addition of CO_2 0 %. The heat release rate had a positive value indicates the presence of heat absorption due to the dissociation of N_2 . Unlike the three other reactions, the reaction $NO+N+O \leftrightarrow N_2$ takes place almost in every z coordinates. There is a gap in the peak value of the reaction about 234.34 W/m^3 between 0–40 % CO_2 . This reaction has a high activation energy of about 318 kJ/mole , due to the triple bond of the N_2 molecule [15]. So along with the decreasing temperature due to the addition of CO_2 , the amount of energy which can be used for this reaction progresses becomes less.

Fig. 4. The heat release rate of some reaction that formed NO at the equivalence ratio of 0.85 in each point: *a* – $NO+N \leftrightarrow N_2+O$; *b* – $N+O_2 \leftrightarrow NO+O$; *c* – $N+OH \leftrightarrow NO+H$; *d* – $N+CO_2 \leftrightarrow NO+CO$

The reaction of $\text{N}+\text{O}_2 \leftrightarrow \text{NO}+\text{O}$ and $\text{N}+\text{OH} \leftrightarrow \text{NO}+\text{H}$ have the same tendency, both reactions showed decreasing values in any additional CO_2 . These reactions are releasing heat that was characterized by the negative value of the heat release rate. The heat release rate of the reaction of $\text{N}+\text{O}_2 \leftrightarrow \text{NO}+\text{O}$ worth $-10\,331\text{ W/m}^3$, whereas the $\text{N}+\text{OH} \leftrightarrow \text{NO}+\text{H}$ reaction worth $-12\,637\text{ W/m}^3$. The differences between the heat release rate without the addition of CO_2 and with the addition of CO_2 40 % on the reaction of $\text{N}+\text{O}_2 \leftrightarrow \text{NO}+\text{O}$ gained about 1489.5 W/m^3 , while the $\text{N}+\text{OH} \leftrightarrow \text{NO}+\text{H}$ reaction was 2223.5 W/m^3 . Although it has a large amount, the occurrence of both reactions in the overall range of z coordinates was quite narrow.

The reaction of $\text{N}+\text{CO}_2 \leftrightarrow \text{NO}+\text{CO}$ had the value of the heat release rate of -463.92 W/m^3 highest at the addition of 40 % CO_2 . There was an increase in the heat release rate of this reaction when the amount of CO_2 added was 40 % that generated about 100.6 W/m^3 indifference. Unlike the three previous reactions, the heat release rate of $\text{N}+\text{CO}_2 \leftrightarrow \text{NO}+\text{CO}$ getting greater along with the increase of CO_2 . This happened because of CO_2 species is one of the reactant species required for this reaction to take place. Among those four reactions, three of these reactions decreased in any addition of CO_2 . Only the $\text{N}+\text{CO}_2 \leftrightarrow \text{NO}+\text{CO}$ reaction is increased with the addition of CO_2 . Even so, the amount of increase gained by the reaction $\text{N}+\text{CO}_2 \leftrightarrow \text{NO}+\text{CO}$ was not very significant when compared with the decline of three other reactions. So from this analysis it can be concluded that the addition of CO_2 will reduce the formation of NO species which can be identified by decreasing the rate of heat release in several reactions that form NO species, as shown in **Fig. 5**.

Fig. 5. NO_2 mass fraction in each equivalence ratio

As seen in **Fig. 5** NO_2 species formed when the equivalent ratio was less than 1. Although the highest temperature gained near stoichiometric, the fewer species NO_2 is formed due to the depleted availability of O_2 species because the species has already reacted with fuel. In the fuel-rich mixture zone, there was no formation of NO_2 . The highest NO_2 mass fraction was 3.07×10^{-6} at an equivalent ratio of 0.62 where the maximum temperature at this point was 1702.2 °K . At the equivalent ratio of 0.56 and 0.5 there was a decline in NO_2 mass fraction, this is due to the lower temperature gained at those equivalence ratio that was about 1588.6 °K and 1486 °K . The following reactions could form NO_2 species:

To determine the effect of CO_2 on this reaction, **Fig. 6** shows a further investigation of the equivalent ratio of 0.62. Analysis was carried out on each addition of CO_2 .

As shown in **Fig. 6**, $\text{NO}+\text{HO}_2 \leftrightarrow \text{NO}_2+\text{OH}$ reaction was releasing the heat in which the highest heat release rate was -3605.09 W/m^3 at the variation without the addition of CO_2 . Along with the addition of CO_2 , the heat release rate continues to decrease until it reached -2509 W/m^3 at the addition of 40 % CO_2 . From the reaction's equation, it can be seen that the formation of NO_2 species is highly dependent on the availability of NO species. So the reaction $\text{NO}+\text{N}+\text{O} \leftrightarrow \text{N}_2$ outline a significant role in the formation of a whole species of harmful NO_x .

Fig. 6. The heat release rate of $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$ reaction at the equivalence ratio of 0.62 in each point

From the results of this study the NO_x species formation are occurs varies in the stoichiometric composition. In the nearly stoichiometric condition (equivalent ratio = 0.85), the highest NO mass fraction gained $3,0598 \times 10^{-3}$ without the CO_2 addition. Meanwhile the 40 % CO_2 dilution could reduce the NO mass fraction down to $2,5235 \times 10^{-3}$. The NO_2 species highest formation gained in equivalence ratio of 0.25 with the NO_2 mass fraction of 3.07×10^{-6} without the CO_2 . By adding 40 % CO_2 the NO_2 mass fraction decreases to 2.84×10^{-6} . The CO_2 dilution was less significant in other equivalence ratio.

Some further investigation still needs to be conducted especially on the NO_x formation at the specific time. By implementing transient analysis, the evolution of the NO_x formation can be investigated thoroughly. In order to achieve the ideal premixed biogas combustion with less dangerous gas species production and enhance the conventional biogas premixed combustion efficiency.

4. Conclusion

1. The decreasing temperature caused by CO_2 addition that more significant on the fuel-rich side. CO_2 does not only decrease the temperature by absorbing heat but also has the potential to make changes in its chemical reactions path. CO_2 dilution could decrease the heat release rate of several reaction that partaking the role in NO and NO_2 species formation.

2. NO_x mass fraction formed only on a fuel-lean mixture of $\text{CH}_4/\text{CO}_2/\text{air}$ and its values decreased along with CO_2 added. The addition of CO_2 could reduce the NO species mass fraction down to 18 %, and NO_2 reduction down to 7 %. This is caused by a decreasing heat release rate of $\text{NO} + \text{N} \leftrightarrow \text{N}_2 + \text{O}$, $\text{N} + \text{O}_2 \leftrightarrow \text{NO} + \text{O}$, $\text{N} + \text{OH} \leftrightarrow \text{NO} + \text{H}$, and $\text{N} + \text{CO}_2 \leftrightarrow \text{NO} + \text{CO}$ reactions. The $\text{N} + \text{CO}_2 \leftrightarrow \text{NO} + \text{CO}$ reaction increased as CO_2 was added but its values were not as much as the decline of three other reactions.

Acknowledgments

Thank you to the Department of Mechanical Engineering, State Polytechnic of Malang, to provide equipment support and be more mature in conducting an analysis.

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Received date 23.12.2020

Accepted date 02.09.2021

Published date 18.11.2021

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How to cite: Susilo, S. H., Wicaksono, H. (2021). Numerical analysis of NO_x formation in CO₂ diluted biogas premixed combustion. *EUREKA: Physics and Engineering*, 6, 57–64. doi: <https://doi.org/10.21303/2461-4262.2021.002072>