



Research article

Numerical simulation of the effect of diluents on NO_x formation in methane and methyl formate fuels in counter flow diffusion flame

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Abstract: The increasing global demand for energy, the need to reduce green house gasses, and the depletion of fossil fuel resources have led for the need for renewable fuel sources such as biodiesel fuels. In the diesel engines, biodiesel fuels can also be used directly without comprehensive engine changes. Biodiesel relates to a diesel fuel that is based on vegetable oil or animal fat consisting of long-chain of methyl, ethyl, or propyl esters. Methyl ester fuel burns more efficiently and has lower emissions of particulate matter, unburnt hydrocarbon, and carbon monoxide than fossil fuels. However, combustion of methyl ester fuel results in increased nitrogen oxides (NO_x) emissions relative to fossil fuels. This study is concerned with characterizing the formation of NO_x in the combustion of methyl formate under a counter diffusion flame. This was carried out in an Exhaust Gas Recirculation (EGR) system. Simulation of the process was done using Combustion Simulation Laboratory Software (COSILAB), and involved simulating the reactions of methyl formate fuel. The results obtained were compared to those of the methane/air diffusion flame, which is a well-characterized system. The extension validated the results obtained for the methyl formate/air diffusion flame. The reduction of NO_x was found to be 26% and 14% in methane and methyl formate diffusion flame respectively from 0% to 29.5% of EGR. Increased EGR from 0% to 29.5% increased NO_x reduction. Compared to methane/air diffusion flame, methyl formate/air diffusion flame with and without EGR had lower NO_x emission. This was found to be true when examining the amount of other metrics viz. temperature, H, OH and N radicals associated with NO_x. This showed that EGR system have an effect on NO_x formation.

Keywords: methane; methyl ester; methyl formate; exhaust gas recirculation (EGR); COSILAB

Annotations

λ : Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$); μ : Coefficient of dynamic viscosity (Ns m^{-2}); ρ : Mass density (kg m^{-3}); cp : Mixture's frozen specific heat capacity at constant pressure ($\text{Jkg}^{-1}\text{K}^{-1}$); c_{pi} : Specific heat capacity at constant pressure for species i ($\text{J kg}^{-1} \text{K}^{-1}$); h_i : Specific enthalpy of species i (J kg^{-1}); L : Lewis number; N : Total number of chemical species present; P : Stress tensor (Pa); p : Hydrostatic pressure (Pa); Pr : Prandtl number; q : Heat flux vector (W m^{-1}); qR : Radiant heat flux vector (W m^{-1}); R : Relating to Radiant heat; R : Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$); s : Specific entropy ($\text{J kg}^{-1} \text{K}^{-1}$); T : Temperature (K); t : Time (s); v : Velocity vector (m s^{-1}); V_i : Diffusion velocity of species i in y direction (m s^{-1}); V_x : Velocity component in x direction (m s^{-1}); V_y : Velocity component in y direction (m s^{-1}); W_i : Molecular weight of species i (kg mol^{-1}); w_i : Rate of production of species i by chemical reactions ($\text{kg m}^{-3} \text{s}^{-1}$); Y : Mass fraction; y : Spatial coordinate (m)

1. Introduction

The main challenges associated with fossil fuels are energy demand increase and environmental pollution. In the last two decades, the use of biodiesel fuel as alternative fossil fuels has increased considerably. Biodiesel fuels lead to lower emissions and reduce dependencies on fossil fuels [1,2]. The use of biodiesel gives higher thermal efficiencies at various engine speeds [3]. Biodiesel fuels typically contain about 10% or higher oxygen content by mass. The presence of oxygen atom in the structure of the biodiesel fuels makes the fuel burn more efficiently with reduced emissions of soot, unburnt hydrocarbons and carbon monoxide [4]. However, combustion of biodiesel fuels produces more oxides of nitrogen (NO_x) compared to fossil fuels [2,5].

Chemical kinetic mechanisms for the combustion methyl formate, a major component of biodiesel have been identified and further developed to capture the production processes of pollutants (NO_x) [6]. These models were then improved with the addition of but research output has been low since these first studies [7]. This is particularly important given that kinetics of combustion of methyl esters have not received much attention in the existing literature. The formation of NO_x has been shown to be high in the methyl esters combusted in a diesel engine system. Among these fuels; methane, methanol and methyl formate, the highest amount of NO_x was obtained in methane and the lowest obtained in methyl formate. These studies were carried out at 1 bar [8,9]. The same trends were observed but NO_x was higher at 50 bars than at 1 bar [10].

The effect of exhaust gas recirculation on diesel engine nitrogen oxide reduction operating with methyl ester derived from jojoba, where the recirculation was done up to 15% and showed a considerable reduction in NO_x formation [11]. The effect of a sustainable biofuel–n-octanol–on the combustion, performance, and emissions of a DI diesel engine under naturally aspirated and exhaust gas recirculation (EGR) modes [12]. Investigation and exploration of the mid-load potential of ethanol–diesel dual-fuel combustion with and without EGR showed a massive reduction of NO formation in the fuels [13]. The effect of high EGR causes low efficiency of a diesel engine and an increase of soot and low combustion of fuels [14]. Hence, there should be more investigations on the optimum and the

right content of exhaust gas recirculated. The study of EGR effect on methyl esters has not gained much interest in research; hence, this research on the effect of diluents using an EGR system on oxygenated fuels. There is a gap in knowledge in reduction of NO_x in methyl ester fuels. In this report this gap knowledge is addressed by studies which provide an optimal EGR rate for minimal NO_x formation in combustion of methyl esters in a model system.

2. Numerical method

2.1. Chemical kinetics of NO_x formation.

Understanding the physical and chemical processes that occur during the combustion of methyl-ester fuels, especially those that greatly influence the formation of NO, is required for the development of better alternatives and design of efficient burners. The four main routes of NO formation in combustion processes are Zeldovich mechanism (thermo NO), N₂O route, prompt NO and Fuel Bound Nitrogen (FBN).

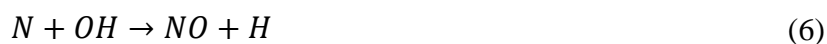
2.1.1. Thermo NO

It is formed at high temperature flame regions through extended Zeldovich mechanism which is shown by Eqs: [15]



2.1.2. Prompt NO

It is formed at low temperature flame front regions due to the presence of CH radicals. The CH radical reacts with molecular nitrogen according to Eq 4. The nitrogen generated from this mechanism proceeds to form NO through Eqs [16]

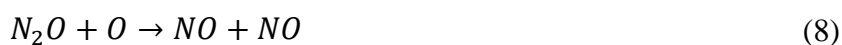


2.1.3. N₂O route

NO production through N₂O route occurs through the free body recombination reactions, Eq 7 under the conditions of high pressures. The N₂O formed in Eq 7 reacts with O to form NO through Eq 8. [16]



Where M is an energy carrier



Combustion of fuels that contain nitrogen results in formation of NO_x . In most of the fuels, including biodiesel fuels used in internal combustion engines, contain a significantly small amount of Fuel Bound Nitrogen and hence Fuel NO_x is neglected in kinetic mechanisms in this research.

2.2. Diffusion flame.

The flow configuration considered is as shown in Figure 1, with the fuel and airside, positioned at the left and right-hand side, respectively. The temperature of both the fuel and air stream was taken as 300 K. The flames were computed at a constant pressure of 1 bar and a strain rate of 50 s^{-1} . At the fuel nozzle, fuel (mole fraction of 1) was specified. The diluents (CO_2) was recirculated through the fuel side in mole fraction of 0% to 29.5% of the exhaust CO_2 and the H_2O is cooled at the EGR cooling system and release as water droplets. At the air nozzle, the mole fractions concentration of O_2 and N_2 were specified using the air standard composition of 0.21 and 0.79 respectively.

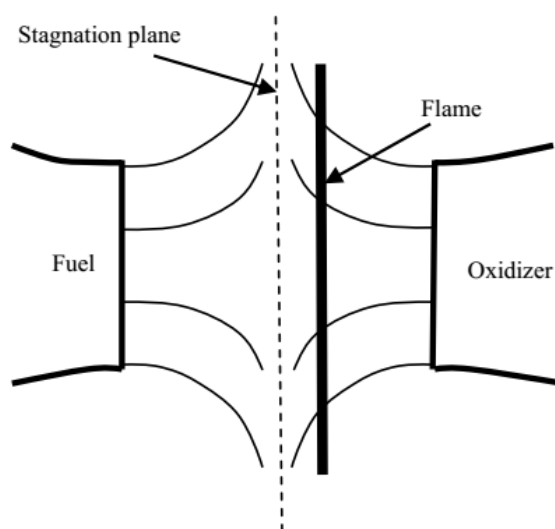


Figure 1. Flow configuration for a diffusion flame [17].

The flame was assumed to be embedded in a thin boundary-layer formed by stagnating flow. Hence, the computation required the use of the boundary layer theory approximations. Though the flame is two dimensional, under this assumption the equations of conservation reduced to one-dimensional forms. Also, the thermodynamic part of the pressure was assumed to be spatially uniform. The effect of viscous dissipation, the Soret and Dufour, and the body forces were neglected. Thus, the governing equations, as derived in [18] are as follows.

$$L_1(1) = 0 \quad (9)$$

$$L_1(G) = \frac{\partial}{\partial y} \left(\mu \frac{\partial G}{\partial y} \right) - \rho G^2 + P'(t) \quad (10)$$

$$c_p L_1(T) = \frac{\partial}{\partial y} \left(\lambda \frac{\partial T}{\partial y} \right) - \frac{\partial T}{\partial y} \sum_{i=1}^N c_{pi} \rho Y_i V_i - \sum_{i=1}^N h_i W_i + \frac{dp}{dt} - \frac{\partial qR}{\partial y} \quad (11)$$

$$L_1(Y_i) = -\frac{\partial}{\partial y} (\rho Y_i V_i) + w_i \quad i = 1, \dots, N. \quad (12)$$

Here L_1 is the accumulative-convective operator given by:

$$L_1(\Phi) = \frac{\partial(\rho\Phi)}{\partial t} + \frac{\partial(\rho V_y \Phi)}{\partial y} + \rho G \Phi \quad (13)$$

The thermodynamic properties (the frozen specific heat capacities at a constant pressure of the pure species i , c_{pi} , the frozen specific heat capacity at a constant pressure of the gas mixture, c_p , and the enthalpy, h_i , for pure species i) were calculated using polynomial curve fits of NASA type [19]. The transport properties required are the dynamic viscosity, μ , and the thermal conductivity, λ , of the gas mixture, which are calculated using the method illustrated in [18].

2.3. Exhaust gas recirculation system (EGR).

Exhausts consist mainly of CO₂, N₂ and water vapor. Through experimental analysis it was found out that the most efficient diluent is CO₂ which decreased NO_x emissions by 64% while Ar and N₂ had an effect of 30% and 58% respectively [20]. When a part of this exhaust gas is re-circulated to the cylinder, it acts as a diluent to the combusting mixture. This also reduces the concentration of O₂ in the chamber of combustion. The EGR's specific heat is much higher than fresh air. Hence EGR increases the heat capacity (specific heat) of the intake charge, thereby reducing the temperature increase in the combustion for the same heat release [21]. The percentage of recirculation can be shown in Eq 14.

$$\text{EGR}\% = \frac{\text{Volume of EGR}}{\text{Total intake charge into the cylinder}} \times 100 \quad (14)$$

2.4. Numerical simulation method

The flames were numerically simulated using the RUN1DL code in the software package [22]. The simulation of methyl formate fuel was done using a developed chemical kinetic mechanism which captures the processes of pollutants [7], while methane fuels used GRI mechanism 2.0 [23]. Conservation equations were discretized with a finite difference method. Both central and one-sided difference (upwind) schemes are adopted in the discretization of first-order derivatives, while the central difference scheme is adopted for the second-order derivatives. For the case of upwind scheme applied to first-order derivatives, the first-order accuracy was achieved. When second-order accurate

central difference scheme was applied to a second-order derivative in a non-uniform grid, one order of accuracy was lost. Numerical accuracy was enhanced by having many grid points in the region of high gradient and having the grids points which were approximately equally spaced. This has been achieved by applying the adaptive selection of grid point technique. Modified Newton method was applied to the resulting nonlinear differential-algebraic equations.

3. Results and discussion

It was found out that the recirculation can only be up to 29.5% of EGR system. The system could only run when the EGR percentage is strictly less than 30%. The software predicted an error in running EGR from 30% and above. This shows that the recirculation cannot exceed 30% of exhaust gas which can hinder combustion of the fuel.

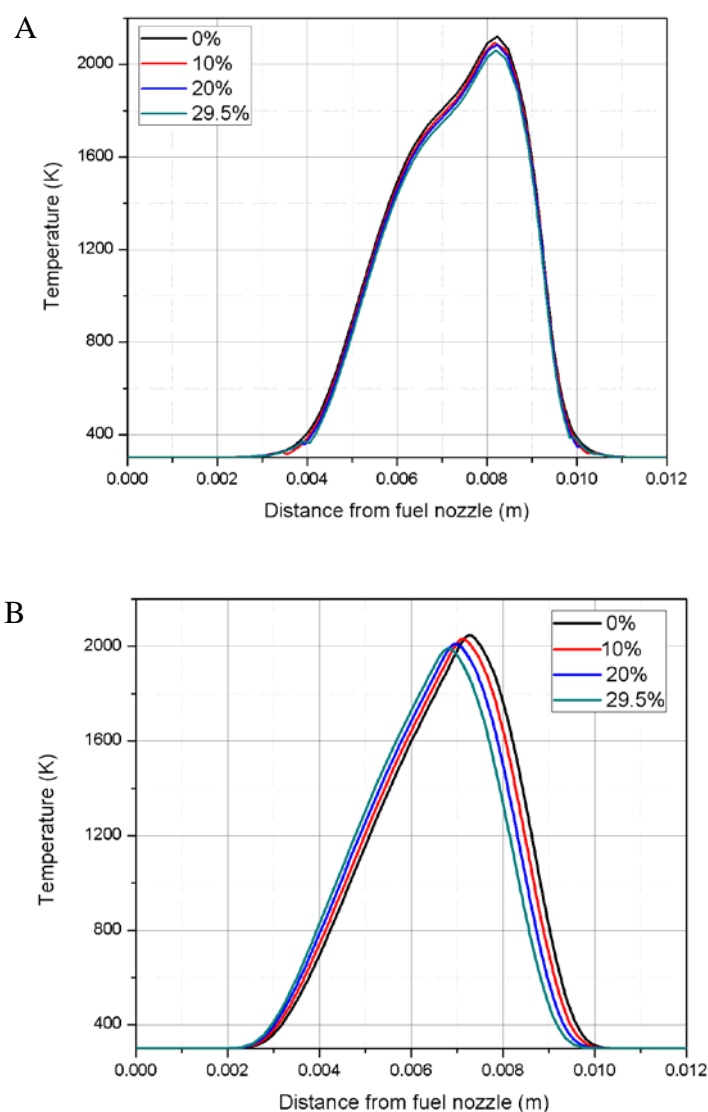


Figure 2. Temperature profile of A: methyl formate/air and B: methane/air diffusion flames.

The production NO_x in combustion is favoured by high combustion temperature [24]. Based on this the temperature profiles for methyl formate/air diffusion flame was simulated at different percentages of varying EGR. The results were compared with that of methane/air diffusion flame. Figure 2 represents temperature profiles of methyl formate/air and methane/air combustion, respectively. The maximum temperature for combustion without recirculation was found to be 2100 K for methyl formate/air and 2050 K for methane/air combustion. Figure 2B shows that with an increase of EGR from 0% to 29.5%, the methane/air diffusion flame, had a reduction in temperature of approximately 58 K while the methyl formate/air diffusion flame had a reduction of 55 K. As EGR was increased the methane/air peak values shifted to the fuel side while the peak values of methyl formate/air did not show a shift only a reduction. Differences in the influence of EGR on the diffusion flame temperature in methyl formate/air compared to methane/air suggest that there are differences in NO_x production in these two different systems.

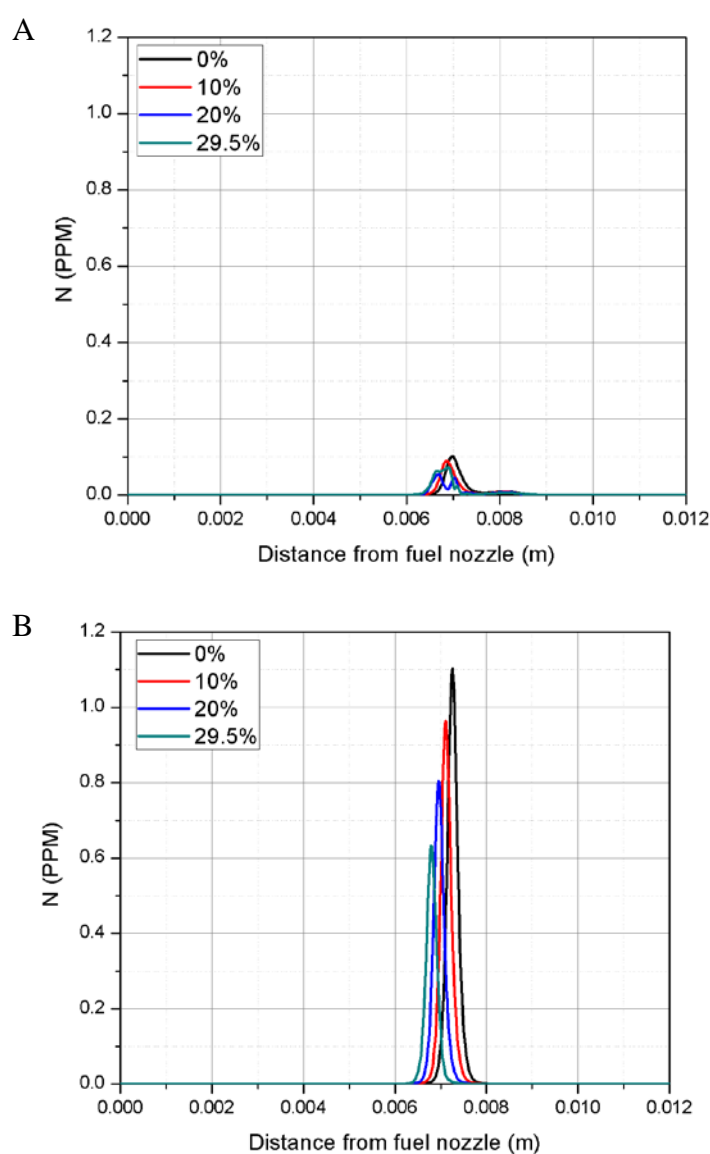


Figure 3. The effect of EGR on N formation in A: methyl formate/air and B: methane/air diffusion flames.

In addition to temperature, radicals of N, O, OH, and CH plays a significant role in prompt-NO and N₂O route in NO_x formation. Hence, the reduction of these species may result in a reduction in the formation of NO_x in the diffusion flames. Figure 3 shows how the mole fractions of N radicals compares to that of methane/air diffusion flame for different amount of EGR. Through reactions: $N + O \rightarrow NO + H$ and $N + O_2 \rightarrow NO + O$ shows that N has a significant impact in formation of NO and with its reduction will have a highly significant reduction of nitrogen oxides. An increase in EGR results in a reduction of N radicals in both methyl formate/air and methane/air diffusion flames, but this decrease is more significant in methane than in methyl formate. The reduction in peak N radical values in methyl formate/air is approximately 0.03 ppm compared to that of methane/air of approximately 0.447 ppm. Similarly there is a shift in both methyl formate/air and methane/air diffusion flames with increasing EGR towards the fuel side. In methyl formate/air diffusion flame peak N radical values were less than those of the methane/air diffusion flame and decreased with increasing EGR showing less NO_x production by EGR recirculation.

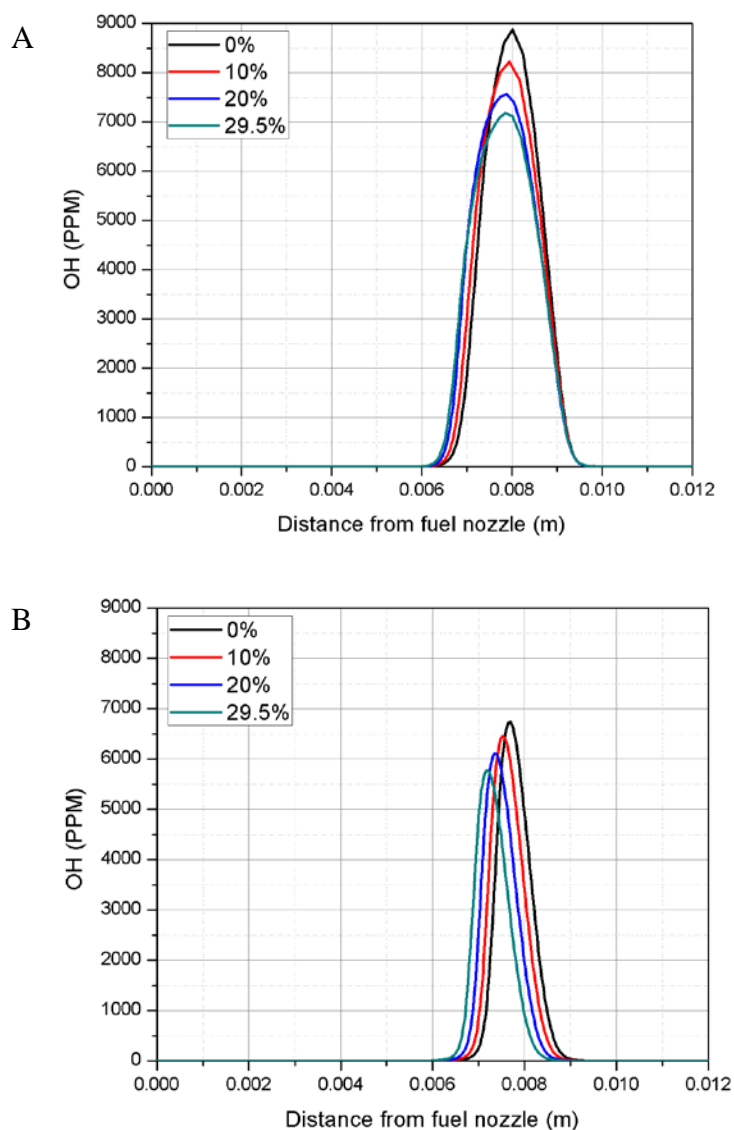


Figure 4. The effect of EGR on OH radical formation in A: methyl formate/air and B: methane/air diffusion flames.

Another important radical in NO_x formation is the OH radical. Figure 4 shows the effect of EGR on mole fractions of OH radicals in parts per million (ppm) in methyl formate/air and methane/air diffusion flames. From the reaction, $N + OH \rightarrow NO + H$ show that OH radical is critical in the formation of NO which is in high quantity; hence, its reduction will reduce the formation of NO. As EGR was increased in methyl formate/air diffusion flame (Figure 4A), the amount of OH radicals decreased. This was the same as the control methane/air diffusion flame. However, methyl formate/air showed a higher reduction in OH radical of approximately 1699 ppm compared to the control methane/air of approximately 962 ppm. The peak values in methyl formate/air diffusion flame shifted towards the fuel side with increasing EGR. This behavior was also observed in methane/air diffusion flame indicating delayed combustion and higher oxygen consumption with increasing EGR. Analysis of OH radicals supports previous observation with N radicals that increasing EGR decreases NO_x formation in methyl formate/air diffusion flame.

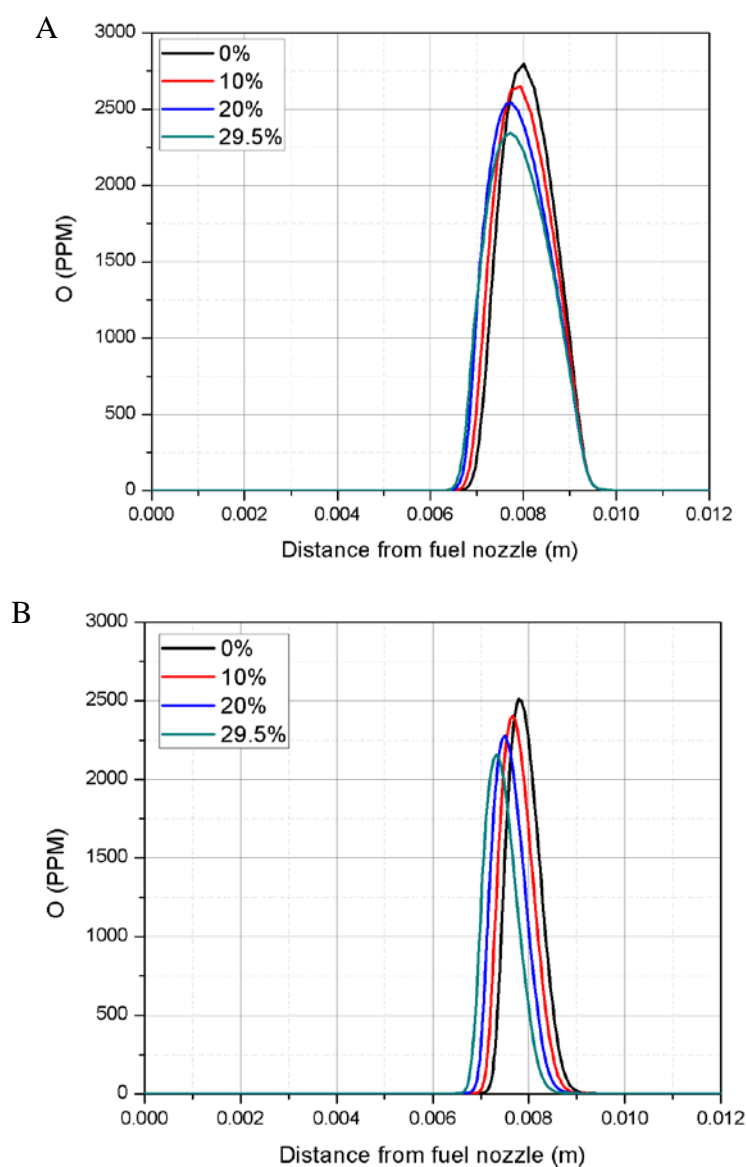


Figure 5. The effect of EGR on O formation in A: methyl formate/air and B: methane/air diffusion flames.

A similar relationship between OH radicals and EGR was observed between O radicals and EGR in methyl formate/air flame. NO formation can also be through $N_2 + O \rightarrow NO + N$. Figure 5 shows how mole fractions of O radicals changed with EGR in methyl formate/air diffusion flame and methane/air diffusion flame. Similar to findings with OH radicals an increase of EGR results in a reduction of O radicals in both methyl formate/air and methane/air diffusion flames, but this decrease is more significant in methyl formate than in methane. The reduction in methyl formate/air is approximately 400 ppm compared to that of methane/air of approximately 300 ppm. Similarly there is a shift in both methyl formate/air and methane/air diffusion flames with increase in EGR towards the fuel side. However, peak values are different between methyl formate/air and methane/air diffusion flame. In methyl formate/air diffusion flame peak O radical values at maximum EGR were higher than those of methane/air diffusion flame. The results demonstrate that NO_x in methyl formate/air diffusion flame can be effectively reduced by EGR. However, the effects of EGR on NO_x are different to that of the widely characterized methane/air system.

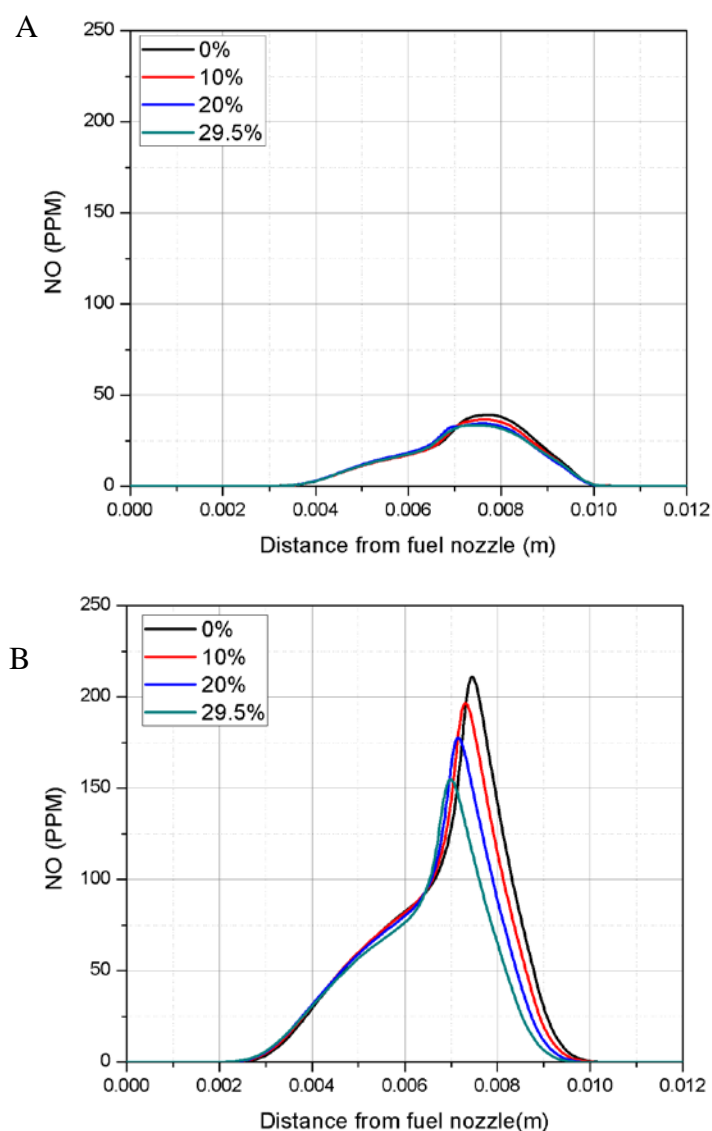


Figure 6. The effect of EGR on the amount of NO produced in A: methyl formate/air and B: methane/air diffusion flames.

One of the reasons for use of EGR in combustion is reduction in NO_x emissions [25,26]. In this research, it was found that with the incorporation of different percentages of EGR the system has a significant reduction in NO_x formation in methyl formate/air system. Figure 6 shows the amount of NO in methyl formate/air and methane/air diffusion flames respectively. There was less NO formed in methyl formate/air compared to that of methane/air; approximately 39 ppm versus 200 ppm respectively without EGR. Similarly with increase in EGR, the amount of NO decreases in both systems but the reduction in peak values was higher in methane/air compared to methyl formate/air; 56 ppm versus 8 ppm. The approximate reduction in peak values from 0% to 29.5% EGR was 26% and 14% in methane/air and methyl formate/air respectively. The difference between methane and methyl formate may be related to decrease in temperatures, O radicals, and OH radicals. Since the flame temperatures were below 2500 K, it is likely that prompt NO was the dominant kinetic mechanism for NO formation.

4. Conclusion

Numerical simulations of NO_x production and reduction in methane/air and methyl formate/air diffusion flame configurations have been investigated. The temperatures attained by diffusion flames favour the production of NO mainly through the prompt NO route [16]. The reduction of the temperature causes a reduced formation of all the species, which in the end reduces the formation of NO, O and OH radicals are produced in high quantities during combustion; hence their reduction has been established as a significant effect of reduction of NO formation. The other minor species investigated and not reported here; N, and CH have an impact on NO formation, and they all reduced significantly. The reduction of temperature and species associated with NO_x suggests a reduction in NO_x formation. Therefore EGR can significantly reduce NO_x in methyl formate combustion.

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Conflict of interest

All authors declare no conflicts of interest in this research paper.

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