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Numerical Study on the Autoignition of Biogas in Moderate or Intense Low Oxygen Dilution Nonpremixed Combustion Systems

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Supporting Information

ABSTRACT: The ignition delay of biogas in mixing layers is investigated using a one-dimensional combustion model, with its application in Moderate or Intense Low oxygen Dilution (MILD) combustion being the focus. The current study reveals the key aspects of the ignition of biogas in a nonpremixed, igniting mixing layer with a hot oxidizer of low oxygen content. The observed characteristics are contrasted against the existing studies on ignition in homogeneous mixtures under similar conditions. Biogas is considered here as a mixture of CH₄ with variable amounts CO₂. The influence of reactive, thermal, and transport properties of CO₂ on the ignition is evaluated using artificial species to mimic the respective characteristics of CO₂. While the ignition delay in homogeneous mixtures shows a strong dependence on CO₂ content in the fuel, the ignition delay predictions from one-dimensional mixing layers show no significant influence of CO₂ levels in biogas. In addition, the influence of oxidizer composition and temperature on ignition delay is determined for CO₂ levels ranging from 0% to 90%. A sensitivity analysis of chemical reactions on the ignition delay shows a negligible effect of CO₂ concentration in biogas. The current study emphasizes the role of oxidizer composition and temperature on the ignition characteristics of a MILD biogas flame.

1. INTRODUCTION

Biogas can be considered as a carbon neutral fuel when it has its origins in the anaerobic digestion of organic matter by living organisms. The major components that make up biogas are methane and CO₂. Due to the presence of a considerable amount of CO₂, biogas has a low calorific value. In spite of this, biogas is a promising candidate to meet the energy targets set by the European Union due to its flexibility as an energy source and its wide range of applications including heating and electricity production. It is widely accepted to be a sustainable fuel for households as well as industrial applications despite challenges with production and implementation. Still, at present, its industrial applications are limited due to low heating value and variable composition of biogas often containing corrosive components such as H₂S. It is not an easy task to ensure the production of biogas with a fixed composition by virtue of its biological origin. The variation in the composition of biogas coupled with its low heat release rate could reduce the thermal efficiency of engines. The application of biogas in engines was reviewed in ref 31. For engine relevant conditions, the ignition delay trend with respect to CO₂ level has been predicted from the studies on ignition of homogeneous mixtures of biogas with air, given that in engine applications biogas is premixed with air. However, for the ignition of biogas in nonpremixed systems where the fuel and oxidizer are initially separated, only limited literature is available to the authors’ knowledge. It is therefore important to extend our knowledge on the influence of biogas composition changes in nonpremixed systems.

For applications such as fueling industrial furnaces, the environmental impact of exhaust gases is a major concern provided that there is a considerable amount of NOx released from conventional burners and so is the carbon footprint left by the fuel consumption. Moderate or intense low oxygen dilution (MILD) combustion has been a subject in a number of studies for its potential to deliver high thermal efficiency with lower pollutant emissions. For achieving MILD combustion, the gas flow has to be kept above the autoignition temperature of the fuel. The fuel is burned under strong mixing in a hot, low oxygen environment. The heat release rate of combustion can be lower than that of conventional feed-back stabilized combustion, provided a hot-diluted environment is maintained. Hence furnaces operating in MILD mode can run on fuels such as biogas with a low heat content. The peak temperatures attained are lower than conventional burners, which yields a substantial reduction in the thermally generated NOx. MILD combustion is materialized in practical burners of various configurations that differ in flame structures and stabilization mechanism. MILD combustion of biogas has been studied using the Delft Jet-in-Hot-Combustion (DJHC) burner, which is a laboratory scale burner that mimics MILD combustion conditions where the fuel jet is issued into a hot coflow of lean combustion products. Oldenhof et al. performed experiments on the DJHC burner with natural gas as the fuel, and Sarras et al. studied the influence of mixing CO₂ with natural gas. The combination of CO₂ and natural gas mimics biogas, except for the presence of trace amounts of ethane and higher alkanes in natural gas. From these studies, the stabilization of JHC flames is found to be dependent on the formation and propagation of autoignition kernels. The ignition delay for methane diluted with CO₂ was experimentally measured for homogeneous mixtures with air by...
Zeng et al.40 Their study focused on the ignition of mixtures with equivalence ratios of 0.5, 1, and 2, for a temperature range of 1300–2100 K and pressure range of 0.1–1 MPa. It was shown that an increase in dilution by CO2 or N2 has an inhibitory effect on ignition delays at every equivalence ratio. This effect is stronger for dilution with CO2 than N2. Their numerical investigation showed that the ignition of methane/air mixtures is sensitive to reactions involving H, O, and OH radicals. With increase in CO2 or N2 in the mixture, reactions promoting the ignition were found to be inhibited. Fischer and Jiang14 performed a computational study on the ignition of homogeneous CH4−CO2−O2 mixtures and compared the ignition delays predicted by five different reaction mechanisms against the results from shock tube experiments. Their study showed that among the five, GRI Mech 3.034 delivered the best predictions for the ignition delays of CH4−CO2 mixtures.

It has to be realized that in a JHC burner the reactants are not premixed. A DNS study on the fine structure of turbulent MILD combustion of methane by Doan et al.12 has shown that the nonpremixed combustion mode is relevant even if the initial mixture is partially premixed. Hence, studies on MILD flames under nonpremixed conditions become necessary to understand their ignition and combustion behavior.5 Sidey and Mastorakos35 studied the effect of adding CO2 to methane in steady diffusion flames under MILD conditions. The effect of strain rate on the flame structure and maximum temperature was studied along with the extinction behavior. Wang et al.38 investigated the chemical and physical aspects of adding CO2 to CH4 in steady counterflow diffusion flames. The CO2 presence was found to reduce the flame temperatures and increase the CO production by reducing its rate of oxidation into CO. These studies on steady diffusion flames provide insights regarding the flame structures, flame quenching, and pollutant formation and help in understanding the interplay of chemistry in MILD nonpremixed flames. However, the ignition in nonpremixed systems was not clearly addressed here which is a key aspect in the flame stabilization in MILD burners.

A one-dimensional Igniting Mixing Layer (IML)1,19,37 serves as the simplest physical representation of a nonpremixed system. The present study aims at investigating the ignition of methane and biogas under MILD conditions through IML simulations. The range of boundary conditions applied in the current study is based on the Delft JHC studies with Dutch Natural Gas (DNG)26 and biogaslike fuels.35 It was found in ref 34 that addition of CO2 did not result in a considerable change of the lift-off height of a natural gas flame, which seems to contradict the findings from studies on homogeneous mixtures where CO2 affects the ignition delays substantially. It was further suggested that the addition of CO2 to natural gas in a JHC may result in a counteracting mechanism of slower ignition chemistry against the increased turbulent entrainment of a hot oxidizer, that maintains the lift-off heights at the same level. The influence of CO2 on ignition is also addressed in the current study. The main objectives of this study are summarized as

- To study the ignition and flame development in an IML and to identify the most sensitive reactions that influence the ignition delay;
- To investigate the effects of CO2 content in the fuel on ignition delay of methane/natural gas and to assess the influence of thermochemical properties of CO2 on biogas ignition;
- To examine the dependence of ignition delay on the oxidizer temperature and oxygen level for CH4 and CH4−CO2 mixtures.

In the following section the computational methodology is presented, the results of IML simulations are discussed next, along with the inferences from sensitivity analysis, followed by the conclusions from the study.

2. COMPUTATIONAL METHOD

The physical and chemical processes in a MILD flame (e.g., JHC) are very similar to those in an IML. An IML is a time-dependent reaction−diffusion layer1,19,37 where the diffusive transport and reactive processes occur simultaneously from an initial unmixed state, which represents a pocket of fuel issuing from the jet and mixing with the hot oxidizer, leading to its ignition. As shown in Figure 1, at time t = 0 for x < 0 the local thermochemical properties describe the fuel flow and for x > 0 they correspond to the oxidizer conditions. Due to the steep initial gradients in concentration of fuel and oxidizer, in the absence of an applied strain, the mixing is governed entirely by diffusive fluxes. The scalar gradients dissipate with time and the reactive−diffusive processes asymptotically approach a state of chemical equilibrium at t → ∞. In the present study, IML is modeled as a time-dependent 1D counterflow flame with a low strain rate (a = 10 s−1). That is, from an initially unmixed state, the mixing layer approaches a steady state counterflow flame with a = 10 s−1. The application of strain rate makes it possible to keep the flame within a physical domain of finite size and to achieve a steady state condition in approximately 1 s. This approach is different from an Igniting Counterflow Flame (ICF)20 where the reactive process starts from a steady nonreacting counterflow solution with an applied strain rate, where the time-dependent changes in scalar dissipation rate is not considered. An IML is expected to mimic a MILD flame than ICF for this reason. The transport equations that describe a one-dimensional unsteady counterflow are given by15

\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} = -\rho G \\
\rho \frac{\partial Y}{\partial t} + \rho u \frac{\partial Y}{\partial x} = -\frac{\partial}{\partial x} \left( \rho U \frac{\partial Y}{\partial x} \right) - \psi = 0
\]  

Figure 1. Schematic diagram of the case setup for IML, representing the initial profiles of the major species and temperature.
\[
\frac{\partial \rho}{\partial t} + \rho \frac{\partial U_i}{\partial x_i} = -\frac{\partial}{\partial x_i} \left( \rho u_i \frac{\partial U_j}{\partial x_j} \right)
\]

(3)

where \(\rho\), \(c_p\), \(\lambda\), and \(\mu\) stand for mass density, specific heat at constant pressure, thermal conductivity, and viscosity, respectively. \(U_i\) represents the diffusion velocity, and \(u_i\) the velocity in \(x\) direction. \(Y_i\) and \(w_i\) are the mass fraction and chemical production rate (kg/m^3.s) of the \(i\)th species where \(i\) ranges from 1 to \(N_{sp}\), the total number of species. The momentum balance in counterflow configuration is modeled after Dixon–Lewis through solving a transport equation for \(G\) (eq 4), the tangential velocity gradient or strain rate:

\[
\frac{\partial G}{\partial t} + \rho u \frac{\partial G}{\partial x} - \frac{\partial}{\partial x_i} \left( \rho u_i G \right) = J - \rho G^2
\]

(4)

Here \(J = \rho_0 \frac{\partial \rho}{\partial t}\), with \(\rho_0\) being the applied strain rate and \(\rho_{ox}\) the density at the oxidizer side. The computational time is set to 1 s within which the flame attains a near steady state. It is assumed that the hot diluted oxidizer is at chemical equilibrium. The oxidizer composition is computed as a constrained chemical equilibrium solution for a given temperature and oxygen level.

In theory, the initial condition for IML can be modeled as a Heaviside function. However, the numerical scheme for resolving diffusive fluxes uses a finite spatial and temporal spacing. Therefore, the Heaviside solution is replaced with a smooth initial condition obtained from a steady counterflow solution with a high applied strain which approximates a Heaviside function. In the current case the initial condition is computed as a steady counterflow solution with \(a = 10^4\) s⁻¹. This applied strain rate is sufficiently high, so that the flame is quenched and initial the mixing layer thickness is of the order of 100 μm. Subsequently, the strain rate \(G(x)\) is rescaled based on \(a = 10^4\) s⁻¹ and the corresponding mass flux \(\rho u\) is updated for every grid point in the domain based on the steady state mass conservation

\[
\frac{\partial \rho u}{\partial x} = -\rho G
\]

(5)

Using the initial profile thus obtained, an unsteady simulation is performed using the one-dimensional flame code CHEM1D. The code uses adaptive mesh refinement in combination with variable time stepping. The results are verified to be independent of mesh size and time step size. For the analysis of the IML flamelet, Bilger’s definition of mixture fraction \(Z\) is used, which is given as:

\[
Z = [0.5M_{H_2}^i[Z_{H_2} - Z_{H_2}] + 2M_{C}^i[Z_C - Z_{C,2}] - M_{O_2}^i[Z_{O_2} - Z_{O_2}]/(0.5M_{H_2}^i[Z_{H_2} - Z_{H_2}] + 2M_{C}^i[Z_{C,1} - Z_{C,1}] - M_{O_2}^i[Z_{O_2} - Z_{O_2}])
\]

(6)

where \(Z_{H_2}, Z_O,\) and \(Z_{C,2}\) are the elemental mass fractions of hydrogen, carbon, and oxygen, respectively. \(M_{H_2}, M_{C},\) and \(M_{O_2}\) are the corresponding atomic masses.

A number of cases with varying fuel and oxidizer boundary conditions is simulated. Table 1 gives a concise overview of the computational set up. On the oxidizer side the temperature \(T_{ox}\) is varied from 1200–1600 K and the oxygen level \(Y_{O_2,ox}\) is varied between 2% and 16% by mass as given in the Supporting Information. The ranges of \(Y_{O_2,ox}\) and \(T_{ox}\) are chosen based on the oxygen percentage and temperature in the coflow of the DJHC experiments. The Supporting Information also gives the mass fractions of major species in the oxidizer and the stoichiometric mixture fraction \(Z_{st}\). The fuel is chosen as methane for the reference case, and for the biogas study, the CO₂ mole fraction is increased from 0% to 90% with the rest being methane. The fuel temperature is chosen as 450 K for all simulations as observed in the DJHC burner. All simulations are performed at atmospheric pressure. A mixture-averaged diffusion transport model is used along with the GRI 3.0 mechanism for reaction chemistry. It was shown in multiple numerical studies that GRI 3.0 gives accurate predictions of ignition delay for biogaslike fuel combinations.

### Table 1. Summary of Computational Setup

| Parameter                | Values                                      |
|--------------------------|---------------------------------------------|
| x range                  | [-1.25] cm                                  |
| time step                | variable time stepping [10⁻⁹:10⁻³] s          |
| number of grid points    | 500 (with adaptive grid refinement)         |
| fuel composition (mol)   | \((1 - X_{C})CH_{4} + X_{CO}CO_{2}\)        |
| fuel temperature         | 450 K                                       |
| oxidizer composition     | vitiated air with \(Y_{O_2,ox} = 0.04\) and 0.06 |
| oxidizer temperature     | 1200–1600 K                                 |
| reaction mechanism       | GRI-Mech 3.0                                 |
| transport model          | mixture averaged                            |

3. RESULTS AND DISCUSSION

First, the characteristics of ignition in an IML are discussed and a comparison of IML is made against ICF. Further, the ignition delay trends for methane and biogas are estimated for a range of CO₂ levels. The impact of CO₂ on the ignition delay of biogas is assessed by introducing artificial species to isolate the effects of chemical, transport, and thermal properties of CO₂. The impact of oxidizer composition and temperature are estimated thereafter. The sensitivity of ignition reactions to the amount of CO₂ in biogas is analyzed under the IML configuration.

3.1. Structure of IML and Comparison with ICF. The evolution of a mixing layer from an unmixed initial condition toward a steady diffusion flame involves a series of mutually dependent chemical and thermal events under a continuously decaying scalar dissipation in the domain. This includes the preignition chemistry, ignition, and heat release followed by diffusion flame spreading. In Figure 2a the time-dependent mixture fraction \(Z\) profiles from \(t = 0\) to 0.1 s in a 1D IML are shown. The fuel considered here is methane, and the oxidizer has 8% O₂ by mass and a temperature of 1540 K. Figure 2a shows the progressive mixing of the initially unmixed fuel and oxidizer, proceeding toward a well mixed state. During the mixing process the hot oxidizer reacts with the fuel releasing heat, and the corresponding temperature profiles are shown in Figure 2b. The temperature rise is defined as \(\Delta T(Z, t) = T(Z, t) - T(Z, t = 0)\). In Figure 2c \(\Delta T(Z, t)\) is plotted against \(Z\); it shows the temperature rise starting from a location with \(Z\) close to 0 and growing to reach a maximum of 600 K near the stoichiometric mixture fraction, \(Z_{st} = 0.02\). The time-dependent variation in the maximum temperature in the...
domain, ΔT_{max} is shown in Figure 2d. It shows a preignition phase where the temperature rise is slow, up to t ≈ 10^{-3} s, and thereafter, ΔT_{max} shoots to a maximum of ΔT_{max} ≈ 600 K owing to a rapid heat release following ignition. Ignition delay under MILD conditions has shown good agreement with a temperature rise threshold of 10 K as it correlates well to the onset of chemiluminescence.\(^{13}\) Hence in this study the ignition delay (τ_{ig}) is defined as the time for achieving ΔT_{max} = 10 K. The value of Z at which this ΔT_{max} is attained is denoted as the most reactive mixture fraction, Z_{mr}.

Autoignition in an IML is governed by reaction and diffusion processes. An unsteady diffusion flame with unity Lewis number is described by the unsteady flamelet equation for temperature as\(^{29}\)

$$\frac{\rho T}{\partial t} = \omega_T + \frac{1}{2} \rho_T \frac{\partial^2 T}{\partial Z^2} \tag{7}$$

where \(\omega_T\) is the source term for temperature from the chemical reactions. The second term in the RHS corresponds to the diffusive transport, with \(\chi\) being the scalar dissipation rate given by

$$\chi = 2D \left( \frac{\partial Z}{\partial x} \right)^2 \tag{8}$$

where D is the scalar diffusivity which is equal to \(\frac{1}{\rho_T}\) for unity Lewis number. A high scalar dissipation delays ignition in nonpremixed systems.\(^{30}\) For an IML with a Heaviside initial condition, the expression for \(\chi\) is obtained as\(^{29}\)

$$\chi(Z, t) = \frac{1}{2\pi t} e^{-2[erf^{-1}(Z)]^2} \tag{9}$$

which indicates that \(\chi \propto t^{-1}\). In order to understand the influence of \(\chi\) on ignition, the IML under consideration is compared against an ICF with the same fuel and oxidizer boundary conditions and with a strain rate of 10 s^{-1}. In Figure 3a the values of \(\chi\) at Z_{mr} and Z_{st} are plotted against time for IML and ICF. Theoretically the values of \(\chi\) in an IML approach infinity at t = 0 as the mixing layer thickness, \(\delta_{th}\), is infinitesimally thin. In this log-log plot, \(\chi_{th}\) follows a straight line with negative slope starting from a magnitude that tends to infinity at t = 0. In the current simulations, the mixing layer thickness \(\delta\) varies from an initial value, \(\delta_{Z,initial} = 0.5\) mm to \(\delta_{Z,final} = 25\) mm. Therefore, the initial values of \(\chi\) are obtained.
to be finite and the final values are determined by the applied strain rate. The red and blue lines correspond to $Z_{mr}$ and $Z_{st}$ respectively. The IML closely follows the $\chi_{th}$ within the range of $\chi$ corresponding to $\delta_{Z_{initial}}$ and $\delta_{Z_{final}}$. The scalar dissipation trend in ICF remains at a constant value as expected. As the flame develops, at $t \approx 1$ ms the exothermic expansion causes a perturbation in $\chi$ for both cases and $\chi$ assumes a lower value following the thermal expansion.

Figure 3b shows the evolution of $\Delta T_Z$, the temperature rise for a constant $Z$ in IML and ICF at $Z_{mr}$ and $Z_{st}$. It can be seen here that the ignition is delayed in the case of IML due to the high value of $\chi$. The delay between $Z_{mr}$ and $Z_{st}$ curves represents the time required for the flame spread. The close proximity of these curves for IML indicates a faster flame spread in the IML. As compared to ICF, IML has a higher $\chi$ during and postignition aiding the flame spread through increased diffusive transport. This is further elucidated in Figure 4 that shows the heat release rate (HRR) contours as a function of mixture fraction and time (until ignition) for (a) ICF and (b) IML. $Z_{st} = 0.02$

Figure 4. Comparison of heat release rate ($W/m^3$) contours as a function of mixture fraction and time (until ignition) for (a) ICF and (b) IML. $Z_{st} = 0.02$

are shown to delay the ignition by more than 2-fold as compared with ICF. The ignition in IML combines the effects of decaying $\chi$ with ignition chemistry; therefore, it mimics the situation in nonpremixed MILD burners better, which is much different from ICF.

3.1.1. Effect of CO2 on the Ignition of Biogas. The ignition of biogas under MILD conditions is estimated in IML simulations with varying levels of CO2 in the fuel. Fuel compositions containing CH4 with CO2 levels that range from 0% to 90% are considered. The $T_{ox}$ is set as 1500 K, with an O2 mass fraction of 8% in the oxidizer. In Figure 5, two ignition time scales are plotted against $X_{CO2}$ for biogas-like fuel compositions. Ignition time scales represented here are the time for $\Delta T = 10$ and 100 K. It shows that the ignition delay remains nearly constant for CO2 levels up to 90% in the fuel. This trend is significantly different from experimentally reported ignition delays in shock tube experiments with uniform mixtures. The additional freedom of chemical species to diffuse across mixture fractions in the case of a nonpremixed flame makes ignition far less sensitive to fuel composition.

Figure 5. Ignition delay against mole fraction of CO2 in fuel.
when compared with homogeneous mixtures. The numerical studies on the ignition of biogas in homogeneous mixtures show CO$_2$ causing significant increase in ignition delays.\cite{40,14} In the mixing layer, however, the influence of CO$_2$ is nearly absent. There is actually a small decrease in $\tau_{fl}$ at higher CO$_2$ levels. After ignition ($\Delta T = 10$ K), the spot of ignition develops into a flame at steady state. For $\Delta T = 100$ K, the slope increases for CO$_2$ levels above 70%. This can be understood from the reduction in heat release rate due to lesser reactive content in the fuel, leading to a slower flame development.

To further explain the observed behavior, the effect of chemical and thermophysical properties of CO$_2$ on the IML ignition delay of biogas is assessed by replacing CO$_2$ in the fuel with the following artificial species as in ref $\text{38}$

1. CO$_2x$, which is chemically inert CO$_2$.
2. CO$_2xx$, which is CO$_2x$ with the diffusivity of methane.
3. CO$_2xy$, which is CO$_2x$ with the heat capacity of methane.

By comparing the ignition behavior of CH$_4$–CO$_2x$ mixtures with CH$_4$–CO$_2$, the influence of reactive properties of CO$_2$ in biogas is assessed. Similarly with CO$_2xx$ and CO$_2xy$, the role of diffusivity and thermal conductivity of CO$_2$ in the ignition of biogas is quantified. In the following analysis and Table 2, the synthetic species CO$_2x$, CO$_2xx$, and CO$_2xy$ replace CO$_2$ at 30% and 90% in biogas and $\tau_{fl}$ is evaluated.

| Table 2. Ignition Delay with CO$_2$ and Artificial Species in IML for $T_{fl}$ = 1540 K and Y$_{O2,fl}$ = 0.08 |
|--------------------------------------------------|
| Ignition delay | $\Delta T_{max} = 10$ K | $\Delta T_{max} = 100$ K |
| CO$_2x$ (ms) | 30% | 90% | 30% | 90% |
| CO$_2xx$ (ms) | 0.97 | 0.91 | 1.38 | 1.57 |
| CO$_2xy$ (ms) | -0.1% | -1.2% | -0.1% | -3.7% |
| CO$_2xy + 0.1%$ | +0.1% | +0.1% | +0.02% | -3.6% |
| CO$_2xy + 0.5%$ | +0.5% | +11.3% | +1.2% | +39.8% |

In Table 2 the first row shows the magnitude of ignition time scales for biogas and the following rows show the change in ignition delays corresponding to each CO$_2$ substitute in comparison with CO$_2$. For cases with CO$_2x$ and CO$_2xx$ the values for $\tau_{fl}$ differ only by $\pm 0.1%$. For CO$_2x$ the ignition delays are slightly reduced, indicating a minute inhibitory influence of CO$_2$ on ignition. These results give a clear proof that the ignition delay is hardly affected by the chemical or transport properties of CO$_2$. As $T_{fl}$ $\approx 10^3$, the CO$_2$ content from fuel can be expected to exert no significant influence on the ignition chemistry. It has to be noted that $\tau_{fl}$ increases slightly for 30% and 90% of CO$_2xy$ in the fuel. This explains that the lower $\tau_{fl}$ at high CO$_2$ levels are a result of the lower heat capacity of CO$_2$ in comparison to CH$_4$. Due to the higher $c_p$ of CO$_2xy$, the flame development delay until $\Delta T = 100$ K is doubled at 90% CO$_2xy$ in comparison with 90% CO$_2$. In the case of CO$_2xx$ the results are much closer to CO$_2x$, showing hardly an impact of transport properties.

3.1.2. Role of Oxidizer Temperature. The influence of oxidizer temperature ($T_{ox}$) on ignition delay is assessed in a series of IMLs subsequently. For a range of $T_{ox}$ the oxidizer composition is computed at fixed values of Y$_{O2,ox}$ = 8%, ensuring the same elemental composition. Figure 6 shows the variation of $\tau_{fl}$ within the given range of temperature. A near linear increase of log($\tau_{fl}$) with respect to the inverse of $T_{ox}$ is observed. It can be noted that the slope of the curve is higher at the lowest temperatures. From shock-tube experiments of methane–oxygen mixtures in argon, an empirical correlation of ignition delay with respect to temperature is given for a range of 1200–2100 K as\cite{11}

$$\tau_{fl}(s) = 2.5 \times 10^{-15} e^{(26700/\Delta T)} [CH_4]^{0.32} [O_2]^{1.02} \text{e}^{(20199/\Delta T)}$$

(10)

where the concentrations of CH$_4$ and O$_2$ are given in moles per cubic centimeter. Equation 10 indicates a linear dependency of log($\tau_{fl}$) on $1/\Delta T$. Furthermore, an increase in O$_2$ concentration shortens the ignition delay and an increase in CH$_4$ concentration increases the ignition delay. Hence, it can be expected that for a counterflow laminar flame with methane and hot oxidizer, the ignition will occur at a mixture fraction close to zero. A comparison of ignition delay trends ($\tau_{fl}$ against $T_{ox}$) can be made for the IML predictions and the empirical relations such as eq 10, based on the experimental observations for homogeneous mixtures. A representative correlation based on eq 10 is given as, $\tau_{fl} \propto [CH_4]^{0.32} [O_2]^{1.02}$\cite{21}. It is assumed here that the [O$_2$] at $Z_{mix}$ is constant, that is, [O$_2$]$_{mix} = [O_2]_{ox}$. The concentration of CH$_4$ is considered at the location of $Z_{mix}$ from the unmixed initial condition. $\tau_{fl}$ is plotted in Figure 6 adjacent to the $\tau_{fl}$ curve for IML using an appropriate scaling constant.

From the experiments conducted by Zeng et al.,\cite{40} a second empirical correlation for $\tau_{fl}$ of methane in homogeneous mixtures is given by

$$\tau_{fl} = 1.31 \times 10^{-3} p^{-0.68} e^{(20199/\Delta T)}$$

(11)

Homogeneous mixtures of methane–air were considered in this study in a temperature range of 1300–2100 K at a mixture equivalence ratio $\phi = 0.5$. In eq 11, $p$ represents the pressure in MPa, which is atmospheric pressure in the current study. The slope of this line is given by, $\tau_{fl} \propto e^{(20199/\Delta T)}$, which is lower than that of $\tau_{fl}$. This trend is plotted in Figure 6, positioned above the ignition delay curve of IML. The IML ignition delay curve shows slope close to the experimentally observed value in eq 11 for most part of the temperature range considered (1300–1650 K). Therefore, the activation temperature, $T_a$ for IML is closer that of $T_a$. For $T_{fl} < 1250$ K ($1000/T_{fl} > 0.8$) the ignition delays are clearly seen to increase in a nonlinear fashion. This region is outside the range of experimental temperatures for $\tau_{fl}$. Here onward the trend gets closer to that from eq 10 until 1200 K ($1000/T_{fl} = 0.83$). Apart from similarity in trends, the magnitude of ignition delays are larger.
in the case of IML compared to the homogeneous mixtures considered here, which is caused by diffusive transport of radical species at the onset of ignition.

Figure 7 shows $Z_{mr}$, the location of $\Delta T_{max}$ in mixture fraction space at the time of ignition, against the oxidizer temperature.

![Figure 7](image)

**Figure 7.** $Z_{mr}$ with respect to $T_{ox}$ for $Y_{O_2,ox} = 0.08$.

It shows that $Z_{mr}$ remains low within the order of $Z \approx 10^{-3}$ but varies across the range of $T_{ox}$. At a high oxidizer temperature, $\tau_{ig}$ is short and the scalar dissipation rates are large, leading to more diffusive transport, causing higher reactivity at $Z > 10^{-3}$. For example, in Figure 4 it was seen in the case of ICF that the heat release and therefore the major reactions are concentrated over a narrow zone close to the oxidizer side, whereas in the IML, the reaction zone is widened as the reactive species are subjected to a high scalar dissipation rate. The radical species formed close to the high temperature zone are transported in the direction of fuel, widening the heat release zone and shifting the $Z_{mr}$ toward $Z_{st}$ compared with ICF. This shift in $Z_{mr}$ however, diminishes with lower $T_{ox}$. With the decrease in $T_{ox}$, the reaction rates slow down leading to an increase in $\tau_{ig}$. Owing to the reduction in scalar dissipation rates with the ignition delay, the $Z_{mr}$ settles toward a limiting value and becomes comparable to ICF.

The ignition delay prediction for biogas compositions are shown in Figure 8 for $Y_{O_2,ox} = 8\%$ in the range of $T_{ox}$ 1200–1540 K. Evidently, for CO2 levels from 0% to 90%, the ignition delay trends and their magnitudes are hardly affected by the presence of CO2. The small change in thermal properties of the fuel is reflected in the small advancement of ignition in the case of biogas with 90% CO2. The relative insensitivity of ignition delays to CO2 levels as observed from Figure 5 holds true for the entire range of oxidizer temperatures considered here.

3.1.3. Role of Oxygen Concentration in Oxidizer. Low levels of oxygen concentration in the oxidizer are a defining characteristic of MILD combustion. Therefore, the dependence of ignition delay with respect to oxygen levels is also investigated here. Figure 9 shows the ignition delay trends to $Y_{O_2,ox}$ of 8% and 4%, for $X_{CO2}$ varying from 0 to 90% at $T_{ox} = 1540 K$. With the oxygen level reduced to half, the ignition delays are seen to be doubled. This is in agreement with the empirical relation 10. With respect to the CO2 level, the reduction in $Y_{O_2,ox}$ does not change the ignition delay behavior as from previous observations. The dependence of ignition delay on $T_{O_2,ox}$ is investigated for oxidizer temperatures of 1200 and 1540 K and for oxygen mass fractions ranging from 2% to 16%. The results are presented in Figure 10. For both the

![Figure 8](image)

**Figure 8.** Ignition delay against $T_{ox}$ for different levels of CO2 in fuel (methane) for $Y_{O_2,ox} = 0.08$.

![Figure 9](image)

**Figure 9.** Ignition delay against percentage of CO2 in the fuel for $Y_{O_2,ox} = 0.04$ and 0.08 with $T_{ox} = 1540 K$.

![Figure 10](image)

**Figure 10.** Ignition delay against oxygen mass fraction in the oxidizer.
oxidizer temperatures, the ignition delay curve remains parallel until the oxygen levels fall below 4%. The dashed lines in Figure 10 represent trends based on empirical relations. The red line is proportional to $[O_2]^{-1.02}$ (eq 10), and the magenta line is proportional to $[O_2]^{-0.3}$, which is chosen to match the trend of the curves. It can be seen that, for $T_{ox} = 1540$ K, the red curve traces the ignition trend until $Y_{O_2,ox} \approx 0.04$ but shows a faster decline in $\tau_{ig}$ with increasing oxygen levels in IML. For $T_{ox} = 1200$ K, the ignition delay in this region increases at a higher order of $[O_2]$ than $-1.02$. At both temperatures (for oxygen levels from 4% until 16%), the $[O_2]^{0.8}$ curve reproduces the trend in $\tau_{ig}$ closely. Hence it can be observed that for IML the ignition delay is less sensitive to the oxygen concentration than in homogeneous mixtures and thereby causing a reduction in the order of oxygen concentration to approximately $-0.8$.

3.1.4. Influence of Trace Amounts of Higher Alkanes. Biogaslike composition considered in the DJHC experiments consists of natural gas (NG) and CO$_2$. NG was used as an affordable alternative to methane in the biogas experiments. The presence of trace amounts of higher alkanes in NG such as ethane and propane are known to reduce the ignition delay of methane, wherein a relatively weak carbon–carbon bond can be thermally split yielding loosely bound hydrogen atoms in the chain initiation step. The ignition of methane–ethane blends are studied in homogeneous mixtures by Aul et al., who indicated that addition of ethane to methane results in a large, nonlinear effect on reactivity and thereby ignition delays. Following ref 32, the presence of higher alkanes in NG is approximated as 3.7% ethane by volume, with the rest of the composition made of 81.3% of methane, 14.4% of nitrogen, and 0.6% CO$_2$. Figure 11 shows the ignition delay comparison for methane and natural gas as the reactive component of biogas, mixed with various levels of CO$_2$. The ignition delay for NG is 10% lower than CH$_4$ due to the presence of C$_2$H$_6$, which accelerates the ignition. However, the addition of CO$_2$ does not show a different interaction with NG than with pure methane.

Figure 12 illustrates the ignition delays in IMLs for methane and natural gas for $Y_{O_2,ox} = 0.08$.

![Figure 11](image1.png)

**Figure 11.** Comparison of $\tau_{ig}$ for biogaslike compositions using natural gas instead of methane with $T_{ox} = 1540$ K and $Y_{O_2,ox} = 0.08$.

![Figure 12](image2.png)

**Figure 12.** Comparison of $\tau_{ig}$ against oxidizer temperature for methane and natural gas for $Y_{O_2,ox} = 0.08$.

In this section, the impact of fuel bound CO$_2$ content on ignition chemistry is examined in IML. Also the influence of oxidizer temperature on the various methane oxidation pathways is evaluated based on reaction sensitivity analysis. The sensitivity of ignition delay to oxidation chemistry of methane and biogas has been examined in previous studies for homogeneous mixtures at specific equivalence ratios. From these studies the influence of CO$_2$ on ignition kinetics is seen to act in two main ways. A first effect is related to the enhancement of the reverse rate of reaction, consuming H radicals which have a positive impact on ignition. The reference to reaction, R99, stands for the corresponding number of the reaction in the GRI 3.0 mechanism. A second mode of influence is related to the increase in third body collision efficiencies. The influence of CO$_2$ on ignition was found to be the largest for a stoichiometric mixture. In the case of IML these equivalence ratios are not isolated and therefore the influences of chemistry on ignition delay needs to be more precise. Also the impact of CO$_2$ on ignition or the reasons for the relative absence of its influence (as seen in previous sections) are investigated. To identify the chemical reactions which are critical to the ignition of biogas in IML, a sensitivity analysis is performed. The sensitivity of ignition delay to the reaction chemistry is examined for oxidizer with 8% O$_2$ and at temperatures of 1200 and 1540 K. IML ignition delays are computed with 10% increment in individual reaction coefficient for every reaction in GRI Mech 3.0. From the results, a relative sensitivity coefficient $\sigma$ for each reaction in the mechanism is computed as

$$\sigma = \frac{k_{r_1} - k_{r_2}}{k_{r_1}} \approx 1 \frac{\tau_{ig}(r_1) - \tau_{ig}}{\tau_{ig} \cdot 0.1}$$

(12)

where $\tau_{ig}(r_1)$ stands for the ignition delay corresponding to a 10% increase in the reaction rate constant $k$ for reaction $r$. A negative value of $\sigma$ points to enhancement of ignition and a positive $\sigma$ denotes an inhibitory effect of the reaction. Figure 13 shows the most sensitive reactions in IMLs plotted for fuels CH$_4$ and CH$_4$–CO$_2$ (90%) corresponding to $T_{ox} = (a) 1200$ and (b) 1540 K. It can be seen that the ignition delay becomes
much more sensitive to reactions at lower temperatures. The reason for this drop in $\sigma$ at high temperatures is the presence of higher amounts of H, OH, and O radicals, which play the main role in chain branching reactions that enhance ignition. Therefore, a 10% change in the most important chain branching reaction in the ignition of alkanes, \( \text{R38} \).
results in less than 10% change in the ignition delay. Therefore, the role of chemistry to rise temperature by 10 K is relatively lower than in case of a low temperature mixture. Furthermore, it can be seen that for the range of temperatures considered, R99, a critical reaction that is important in homogeneous mixtures of biogas, has no notable influence on the ignition delay. This could be due to the fact that despite containing 90% CO2 in the fuel, at Zmr the CO2 levels are not high enough to cause a reversal in reaction R99.

Considering the third body collision efficiency aspect of CO2, Fischer and Jiang14 found that the thermal decomposition of methane by means of reaction

\[
\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}
\]  \hspace{1cm} (R38)

becomes crucial for rich homogeneous mixtures in the presence of CO2. In the case of IMLs, however, this reaction shows very low sensitivity, (\(\sigma < 0.3\%\), this reaction is therefore not included in the figures comparing the sensitivity coefficients) as again Zmr is situated in an ultralean region in mixture fraction space. Hence the presence of CO2 is seen to be irrelevant on ignition kinetics.

Further, the response of oxidation steps for methane to the oxidizer temperature is addressed. It can be seen from Figure 13 that the chain branching reaction R38, which plays the most important role in ignition, promotes ignition at \(T_{\text{ox}} = 1540 \) and 1200 K. The instantaneous rates for major reactions inhibiting and promoting ignition are plotted as a function of Z in Figure 14 for both fuels under consideration. Although it does not provide direct information on the history of reactions, it gives insight into the reaction rates at the time of ignition indicating the fuels’ stage of oxidation. It can be noted that at 1200 K the heat release is of much lower magnitude and takes place at much lower mixture fraction than for 1540 K. As previously discussed in section 3.1.2, this effect is caused by the scalar dissipation decay in IML. Also methane shows ignition closer to the oxidizer than biogas (with 10% methane). The reduced availability of methane shifts the heat release to a region away from the oxidizer.

In the C1 branch for the oxidation of methane, two reaction paths exist for the conversion of CH3 into CO2:21,38

\[
\text{CH}_3 \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2
\]

\[
\text{CH}_3 \rightarrow \text{CH}_2(\text{s}) \rightarrow \text{CH}_2 \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2
\]
R97 and R119, which are among the most ignition promoting reactions in Figure 13, mark the distinct reaction lines for CH3.

$$\text{OH} + \text{CH}_3 \rightarrow \text{CH}_2(S) + \text{H}_2\text{O} \quad (R97)$$

$$\text{HO}_2 + \text{CH}_3 \rightarrow \text{OH} + \text{CH}_2\text{O} \quad (R119)$$

Figure 13 shows the instantaneous rates of R97 and R119 at ignition. From the plots, the reaction rate of R119 is higher than R97 at 1200 K for both fuels. The sensitivity coefficients show that ignition is highly promoted by R119 at 1200 K, in comparison to which R97 shows a lower ignition promoting effect. R119 is known to be the dominant oxidation step for methyl radical close to ignition, $^{21,41}$ producing the dominant chain branching radical OH and CH3O, at the same time-consuming HO2. As for homogeneous mixtures, this reaction is shown to be highly ignition promoting. $^{41}$ R119 competes with the chain termination reactions, R87 and R158

$$\text{OH} + \text{HO}_2 \leftrightarrow \text{O}_2 + \text{H}_2\text{O} \quad (R87)$$

$$\text{CH}_3 + \text{CH}_4 + \text{M} \rightarrow \text{C}_7\text{H}_6 + \text{M} \quad (R158)$$

competing for HO2 and CH3, respectively. The highest ignition inhibiting effect (largest positive values of $\sigma$) for R87 and R158 at 1200 K highlights the significance of reaction R119 in the case of IML as well. Furthermore, the ignition inhibiting reactions mainly show one characteristic, that is the formation of HO2, feeding reaction R87 at 1200 K.

The ignition promoting reactions with highest $\sigma$ indicate dominance of the second reaction line in the C1 branch. At $T_{\text{ex}} = 1540$ K, R97 has a higher reaction rate than R119 and has a higher ignition promoting effect in comparison. Here the inhibitory effect of chemistry on ignition becomes much smaller in general and the inhibitory influence of HO3 forming reactions are seen to be diminished. Further down the pathway, reaction R290

$$\text{CH}_3 + \text{O} + \text{M} \rightarrow \text{H} + \text{H} + \text{CO}_2 \quad (R290)$$

shows maximum sensitivity. Furthermore, Figure 14a, b shows that the peaks of R97 and R290 are aligned at both temperatures to the HRR peak, whereas the peak of R119 is offset to the richer side at high temperature. At high temperatures, shorter $t_{\text{in}}$ cause ignition to occur under high $\chi$ (Figure 7), which favors diffusion to the richer side, hence shifting the peaks of reactive species. Here R97 shows lesser influence of $\chi$ as compared to R119. This suggests that R97 is a more significant route of oxidation for methyl radical at high temperature and scalar dissipation rate.

The subsequent oxidation of CH2(S) results in the formation of formyl radical and its conversion to CO could take place following the reaction pathways R167 and R168,$^{36}$

$$\text{HCO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M} \quad (R167)$$

$$\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \quad (R168)$$

Figure 13b shows that R167 promotes ignition whereas R168 has a high inhibitory effect on ignition as it produces the chain terminating radical HO2. Figure 14c, d shows that R168 has a higher reaction rate than R158 and R87 which are the most ignition inhibiting reactions at 1200 K. The relative increase in the influence of HCO oxidation at 1540 K suggests that the ignition is more sensitive to the terminal steps of methyl oxidation at high temperatures.

From the observations comparing ignition chemistry at 1200 and 1540 K in Figure 14, it can be suggested that following the main chain branching reaction R38, at 1200 K the ignition is promoted by the methyl oxidation route R119 and inhibited by R87 and R158. R97 promotes ignition better at 1540 K and the inhibitory effect of HO2 producing reactions on ignition are at bare minimum here. The shift in the most sensitive reaction pathways across temperatures indicates the stage of flame development at which ignition is attained. In the case of IML, for both oxidizer temperatures considered, the influence of CO2 on ignition sensitivity can be attributed to the heat capacity of CO2 rather than its chemical depletion of the O/H radical pool which is critical for ignition as seen in homogeneous mixtures. Therefore, it is shown here that fuel bound CO2 is irrelevant to the ignition chemistry. The sensitivity coefficients for methane oxidation steps show that in a nonpremixed environment the reaction pathways changes their sensitivities with respect to the oxidizer temperature.

4. CONCLUSION

The ignition of methane and biogas in unsteady reaction—diffusion layers (IML) was investigated. In contrast with previous studies on the ignition of biogas in homogeneous mixtures, $^{14}$ the current study shows that the addition of CO2 has little influence on ignition delay in nonpremixed mode. The largest influence of CO2 addition is found in the flame spreading rate, that is, an increment in CO2 level leads to a slower growth of the flame across the mixture fraction space. The differences between the ignition in a spatial mixing layer and a counterflow setup are also studied. Against ICF, IML shows increased ignition delay due to high initial scalar dissipation rate. It is shown in the results that in a nonpremixed MILD environment, the properties of the hot oxidizer impart a far more significant influence on ignition delay than the inert components in biogas. A sensitivity analysis of ignition delay with respect to CO2 levels in biogas shows weak relative sensitivity with respect to reactions involving any of the fuel components.

The results from the current study are important for modeling turbulent MILD combustion of biogas. This holds especially for of a Jet-in-Hot-Combustor burner where the turbulent mixing of fuel with the hot coflow leads to pockets of ignition, which stabilizes the flame. With respect to MILD combustion in practical applications, further investigation is required to understand the role of product recirculation, interaction of multiple mixing layers, higher dimensional effects, and turbulence on the ignition of biogas in non-premixed systems. The influence of turbulence on non-premixed ignition was reviewed by Mastorakos.$^{23}$ An increase in the CO2 content in biogas increases $Z_{\text{in}}$ and, therefore, may enhance the effects of turbulence on ignition. The results from the current IML study helps in explaining the experimental findings in DJHC experiments with biogas, that a higher level of CO2 in the fuel may not affect the ignition delay and thereby the lift-off height of the flame.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b01388.

Table of oxidizer boundary conditions as mentioned in the text (PDF)
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NOMENCLATURE

\( a \) = strain rate
\( c_p \) = specific heat capacity
\( D \) = scalar diffusivity
\( G \) = tangential velocity gradient
\( i \) = index of chemical species
\( k_r \) = reaction rate
\( M \) = atomic mass
\( N_{sp} \) = total number of species
\( p \) = pressure
\( t \) = time
\( T \) = temperature
\( T_{oa} \) = oxidizer temperature
\( U_i \) = diffusion velocity
\( w_i \) = net chemical production rate
\( X_i \) = species mole fraction
\( Y_{O,oa} \) = oxygen mass fraction in the oxidizer
\( Y_i \) = species mass fraction
\( Z \) = mixture fraction
\( Z_{mu} \) = most reactive mixture fraction
\( \Delta T \) = temperature rise
\( \Delta T_z \) = temperature rise along a constant mixture fraction
\( \text{erfc} \) = complementary error function
\( \chi \) = scalar dissipation rate
\( \delta \) = mixing layer thickness
\( \lambda \) = thermal conductivity
\( \mu \) = viscosity
\( \rho \) = density
\( \rho_{oa} \) = oxidizer density
\( \sigma_r \) = relative sensitivity
\( \tau_{ig} \) = ignition delay

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