Fuel 211 (2018) 898–905

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

The use of CO_2 as an additive for ignition delay and pollutant control in CH_4/air autoignition

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ARTICLE INFO

Keywords:
Autoignition
NO
Methane
CSP

ABSTRACT

The effect of CO_2 dilution on the adiabatic and isochoric autoignition of CH_4/air mixtures is analyzed with Computational Singular Perturbation (CSP) algorithmic tools, with a particular emphasis on the determination of the features of the chemical dynamics that control ignition delay and emission formation. Increasing CO_2 dilution causes longer ignition delays, lower final temperatures and decreased formation of NO and CO. These effects of CO_2 dilution are shown to be entirely thermal, contrary to what happens with dilution with H_2O, which also has chemical activity and can reduce ignition delay. For the same initial mole fraction of the diluent, the decrease in final temperature and in NO concentration is larger in the CO_2 case whereas the decrease in CO is larger in the H_2O case. The thermal effect of CO_2 is entirely analogous with those of dilution with the chemically inert Ar, only stronger for the same percentage of initial dilution, because of the larger specific heat of CO_2. The reactions that have the largest contribution to the characteristic explosive time scale of the system during ignition delay ($H_2O_2(+M) \rightarrow OH + OH(+M)$, $CH_3O_2 + CH_2O \rightarrow CH_3O_2H + HCO$, $CH_4 + CH_3O_2 \rightarrow CH_3 + CH_3O_2H$, $H + O_2 \rightarrow O + OH$, etc.) are not substantially affected by CO_2 dilution, neither are the species that are pointed by CSP (CH_3O_2, H_2O_2, CH_2O, etc.) as having the largest impact on the this timescale. The same holds for the modes that control CO and NO formation. The results point to the possibility of cold exhaust gas recirculation being used in order to produce mixtures with longer ignition delays and therefore substantial resistance to uncontrolled ignition.

1. Introduction

Over the last three decades, emission reduction (especially with respect to NOx and soot) has emerged as the major criterion of internal combustion engine design. One of the main tactics that has been employed to this purpose is exhaust gas recirculation (EGR). Basically, EGR involves introducing into the combustion chamber CO_2 with or without water vapor, depending on whether water has condensed during the process. In the early work of [1], a first explanation was provided for the experimentally established fact that CO_2 dilution drastically reduced NOx emissions, which was solely thermal; CO_2 is an almost inert gas with relatively large specific heat, thus it can decrease final combustion temperature and affect the formation of thermal NO [2], which in most practical applications is the main source of NOx. The phenomenon was systematically studied in [3] where it was shown that the dilution effect of CO_2 is dominant over the one of water because of the larger quantity of CO_2 in the exhaust gases and the relatively higher specific heat of CO_2. Recently, it has been suggested that the way CO_2 works is not purely thermal but may also be chemical and entail changes in the concentration of species and radicals that are involved in NOx formation [4], although the specific chemical paths have not been identified. Several potential disadvantages of CO_2 dilution have also been pointed out, such as increased hydrocarbon emissions and lower thermal efficiency due to lower final temperatures [5,6]. These findings led to different opinions as to whether hot or cold EGR was preferable [6,7]. The engine experiments are also supported by experimental and numerical studies in idealized burners that discussed the effect of CO_2 dilution on laminar and turbulent flame speed [8,9]. The consensus was that the effect of CO_2 was mainly thermal and it may be accompanied by some, mostly unspecified, chemical activity.

The recent development of low-temperature combustion technologies that aspire to reduce emissions through flameless combustion in homogeneous (or, at least, partially premixed) mixtures has cast a completely new light in the potential utility of EGR. This is because the main hurdle for the practical application of such technologies is accurate control of ignition timing [10]. The hot gases of EGR can in

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http://dx.doi.org/10.1016/j.fuel.2017.09.022
Received 6 April 2017; Received in revised form 28 June 2017; Accepted 7 September 2017

principle be readily available additives to the mixture of reactants that can be used for this purpose. In fact, in the pioneering work of [11] it was concluded that "CO_2 showed the best promise in terms of ignition timing control". The experimental observations of [11] supported the hypothesis in [4] that CO_2 may also have some chemical activity, but the ways through which this is realized remain unidentified.

In a recent paper [12], we have explored the way in which the other main component of EGR, i.e. water vapor, affects NOx emissions and ignition delay and we were able to show that H_2O acts not only as a thermal buffer but it also enhances reactivity through the reaction $H_2O_2 + (H_2O) \rightarrow OH + OH + (H_2O)$, which we were able to identify algorithmically using tools derived from the Computational Singular Perturbation (CSP). CSP is an algorithmic method for the analysis of systems with multi-scale dynamics, which we have used in previous works in order to analyze oxidation dynamics [12–14]. In this paper, we expand on the work of [12] and we use CSP in order to determine the effect of CO_2 addition on NOx emissions and ignition delay. Our target is to identify the effect of CO_2 on the reactions that contribute the most to the modes of the dynamics that drive the system to explosion. A first issue of particular importance is the comparison with the way in which H_2O acts, because it has been suggested based on the experimental results of [3,10,15] that CO_2 has a stronger effect than H_2O. Another one is to compare, similarly to the H_2O case, the relative importance of thermal and chemical effects. It is noted that the methodology that is developed here can also be instrumental in the analysis of oxy-fuel combustion [16]; i.e. combustion with pure oxygen that is diluted with CO_2, which is a technology that has recently attracted renewed interest because it can be combined with carbon capture. Of course, such combustion has very limited NOx issues, but the tools that we develop can be utilized in order to study ignition delay, CO, and unburned hydrocarbon emissions in oxy-fuel combustion.

The structure of the manuscript is as follows. First, the CSP tools employed will be introduced. Considering homogeneous, constant volume, adiabatic CH_4/air autoignition, the major effects of the CO_2-dilution will be discussed and compared with those of the H_2O and Ar-dilution. The dynamics of CO_2-diluted CH_4/air autoignition will be examined and the reactions and species related most to the explosive time scale will be identified. Finally, the modes that relate to the NO and CO production after the steep temperature rise will be analyzed.

2. The CSP tools

The adiabatic isochoric autoignition of homogeneous methane/air mixtures is examined. Pure mixtures, as well as mixtures diluted with CO_2, H_2O and Ar are considered at various starting temperatures $T(0)$, an initial pressure $p(0) = 3$ MPa and equivalence ratio $\phi = 0.8$, which correspond to typical conditions prevailing in burners related to energy conversion. The chemical kinetics mechanism employed consists of $N = 198$ species, $E = 7$ elements (O, H, C, N, He, Ar and S) and $K = 1330$ reversible reactions and has been validated in a wide range of conditions ($\phi = 0.5, 1.0, 2.0$ and up to 28 atm) [17]. When the forward and backward directions of the K elementary reactions are considered as separate unidirectional ones, the governing equations are:

$$\frac{d}{dt}\begin{bmatrix}\mathbf{y}\\ T\end{bmatrix} = \frac{1}{\rho}\begin{bmatrix}\mathbf{W}\\ \frac{1}{c_v}(-\mathbf{h}_c\cdot\mathbf{W} + RT\mathbf{U})\end{bmatrix}\sum_{k=1}^{2K}\mathbf{S}_kR^k = \sum_{k=1}^{2K}\hat{\mathbf{S}}_kR^k \qquad (1)$$

where $\mathbf{y}$ is the N-dimensional column vector of the species mass fractions, $\mathbf{S}_k$ and R^k represent the N-dim. stoichiometric vector and reaction rate, respectively, of the kth unidirectional reaction, ρ is the mixture density, $\mathbf{W}$ is a $N \times N$ diagonal matrix with the species molecular weights in the diagonal, c_v is the specific heat under constant volume, $\mathbf{h}_c$ is the N-dimensional vector of the species absolute enthalpies, T is the temperature, R is the universal gas constant, $\mathbf{U} = [1,\ldots,1]$ and $\hat{\mathbf{S}}_k$ is the generalized kth $(N+1)$-dim. stoichiometric vector [18]. Eq. (1) can be cast in CSP form as:

$$\frac{d\mathbf{z}}{dt} = \sum_{n=1}^{N-E+1}\mathbf{a}_n f^n = \mathbf{g}(\mathbf{z}) \qquad (2)$$

where $\mathbf{z} = [\mathbf{y},T]^T$ is the $(N+1)$-dim. state column vector, $\mathbf{a}_n$ is the $(N+1)$-dim. CSP column basis vector of the n-th mode, f^n is the related amplitude $f^n = \mathbf{b}^n\cdot\mathbf{g}(\mathbf{z}), \mathbf{b}^i\cdot\mathbf{a}_j = \delta^i_j$ and $\mathbf{b}^i$ is the $(N+1)$-dim. row i-th dual basis vector [19,20]. The amplitudes f^{N-E+2} to f^{N+1} represent the conservation of the E elements and are by definition zero. When the M fastest time scales (τ_1 to τ_M) of the system in Eq. (2) are exhausted, the system reduces to:

$$f^m \approx 0 \quad (m = 1,\ldots M) \qquad \frac{d\mathbf{z}}{dt} \approx \sum_{n=M+1}^{N-E+1}\mathbf{a}_n f^n \qquad (3)$$

The M-dimensional algebraic system $f^m \approx 0$ defines a low dimensional surface in phase space, known as Slow Invariant Manifold (SIM), on which the solution evolves according to Eq. (3). When the solution evolves sufficiently far from the boundaries of the SIM [21], this system of ODEs governs the slow evolution of the process, is free of the M fast time scales and its dynamics is characterised by the fastest of the slow $(N{-}M{-}E + 1)$ time scales [20]. In this work, the CSP basis vectors $\mathbf{a}_n$ are approximated by the right eigenvectors $\boldsymbol{\alpha}_n$, which provide leading order accuracy [19].

The action of the n-th CSP mode $\mathbf{a}_n f^n$ is assessed by (i) its characteristic time scale τ_n (specifies the time frame of its action), (ii) its amplitude f^n (determines the impact of its action) and (iii) the variables that relate to this mode. Considering the case when λ_n is real (the extension to complex pairs is straightforward [22]), the time scales are approximated by the relation $\tau_n = |\lambda_n|^{-1}$ $(n = 1,\ldots N{-}E + 1)$, where λ_n is the n-th non-zero eigenvalue of the Jacobian $\mathbf{J}$ of $\mathbf{g}(\mathbf{z})$. When λ_n is positive (negative), the related time scale τ_n is an explosive (dissipative) one, since it relates to components of the system that tend to lead it away from (towards to) equilibrium. The eigenvalue is defined as $\lambda_n = \boldsymbol{\beta}^n\cdot\mathbf{J}\cdot\boldsymbol{\alpha}_n$, where $\boldsymbol{\alpha}_n$ and $\boldsymbol{\beta}^n$ are the n-th right (column) and left (row) eigenvectors of $\mathbf{J}$, respectively. The n-th eigenvalue can be expressed as:

$$\lambda_n = \boldsymbol{\beta}^n\cdot\sum_{k=1}^{2K} grad(\hat{\mathbf{S}}_kR^k)\cdot\boldsymbol{\alpha}_n = c_1^n + \cdots + c_{2K}^n \qquad (4)$$

since $\mathbf{J} = grad(\hat{\mathbf{S}}_1R^1) + \cdots + grad(\hat{\mathbf{S}}_{2K}R^{2K})$ [18,23,24]. The *Time scale Participation Index* (TPI) is derived from the expression in Eq. (4) as:

$$J_k^n = \frac{c_k^n}{|c_1^n| + \cdots + |c_{2K}^n|} \qquad (5)$$

where $n = 1,\ldots N{-}E + 1, k = 1,\ldots 2K$ and by definition $\sum_{k=1}^{2K}|J_k^n| = 1$ [23]. J_k^n measures the relative contribution of the k-th reaction to λ_n and, therefore, to τ_n. A positive (negative) J_k^n implies that the k-th reaction contributes to the explosive (dissipative) character of the n-th time scale τ_n. Here, the Jacobians $\mathbf{J}$ and $grad(\hat{\mathbf{S}}_kR^k)$ are computed from algebraic expressions. Given the expression for the amplitude f^n:

$$f^n = \mathbf{b}^n\cdot(\hat{\mathbf{S}}_1R^1 + \cdots + \hat{\mathbf{S}}_{2K}R^{2K}) = d_1^n + \cdots + d_{2K}^n \qquad (6)$$

the contribution of each reaction to f^n is measured with the *Amplitude Participation Index* (API):

$$P_k^n = \frac{d_k^n}{|d_1^n| + \cdots + |d_{2K}^n|} \qquad (7)$$

where by definition $\sum_{k=1}^{2K}|P_k^n| = 1$ [20]. For the slow modes $(n > M)$, P_k^n measures the relative contribution of the rate of the k-th reaction to f^n. Since by construction $f^n > 0$, a positive (negative) value of P_k^n denotes a tendency of the k-th reaction to increase (decrease) the impact of the n-th mode. Finally, the variables (mass fractions or temperature) that (i) relate the most to τ_n and (ii) are functionals in the reaction rates that contribute to τ_n and f^n are identified with the *CSP Pointer* (Po), which is defined as:

$$\mathbf{D}^n = diag[\boldsymbol{\alpha}_n\boldsymbol{\beta}^n] = [\alpha_n^1\beta_1^n,\ldots,\alpha_n^{N+1}\beta_{N+1}^n] \qquad (8)$$