# Ignition delay control of DME/air and EtOH/air homogeneous autoignition with the use of various additives

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## HIGHLIGHTS

- The autoignition of DME/air and EtOH/air mixtures is analyzed.
- The relation of the intermediates to the ignition delay is assessed.
- Species closely related to ignition delay are selected as additives.

## ARTICLE INFO

## ABSTRACT

The effect of selected additives on the ignition delay of ethanol (EtOH)/air and dimethylether (DME)/air mixture is investigated. Computational Singular Perturbation (CSP) tools are utilized in an effort to determine algorithmically which species to select as additives and it is established that CSP can identify species whose addition to the mixture can affect ignition delay. However, this is not a necessary condition for additives to be effective. Additives that are not identified by CSP can have a substantial effect on ignition delay, provided that they drastically alter the prevailing chemistry, by altering the instant in time when the thermal runaway regime develops. Some of the additives that were studied computationally are unstable radicals whose injection in practical mixtures is unrealistic. However, chemically stable, relatively light species were also determined that can drastically affect ignition delay, such as hydrogen peroxide, formaldehyde and acetaldehyde.

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## 1. Introduction

Researchers of internal combustion engines have coped for decades with a substantial challenge. Although the need for increased efficiency has consistently generated a motive to operate with high compression ratios in compression-ignition ("diesel"-type) engines, the complicated balance between NOx and soot emissions in these engines has generated serious environmental concerns. A recent set of technologies that aspire to address this challenge are the so-called Low-Temperature Combustion (LTC) technologies, with Homogeneous Charge Compression Ignition (HCCI), Premixed Charge Combustion Ignition (PCCI), and partially premixed combustion being the most common among them. The idea behind these technologies was to generate a homogeneous, possibly flameless combustion at relatively low temperature so that formation of NOx was avoided. At the same time, the relatively long ignition delays associated with lower temperatures would provide the

necessary time for good mixing, which would allow for simultaneous reduction of soot emissions. These potential advantages were demonstrated experimentally and computationally in a series of studies in the '00s and the '10s, of which Refs. [1–10] constitute a representative sample. A thorough review of HCCI-related work was provided in Ref. [11], whereas the potential of combining these clean combustion technologies with possibly renewable biofuels generated a vigorous excitement [11–14].

However, industrial application of these novel combustion technologies has so far not been possible because of the lack of reliable mechanisms to control ignition and heat release rate. For example, in HCCI combustion practically happens at constant volume, which can lead to rapid heat release and pressure increase that may perturb the engine operation [11,15]. Because these combustion technologies miss an external ignition source (that would generate unwanted high-temperature flamelets), ignition is left solely to the complicated dynamics of the oxidation process. This realization has actually motivated R. Reitz and his collaborators to propose the so-called Reactivity Controlled Combustion Ignition (RCCI), which basically entails blending additives into the fuel for

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the purpose of controlling the ignition delay. The idea and the progress on it is reviewed nicely in Ref. [15]. Initially, blends were proposed of fuels of relatively low and relatively high reactivity, while later additives were suggested that could affect the cetane number of the fuel such as DTBP (di-tertiary butyl peroxide). This was of course part of a broad line of research in fuels additives that included alcoholic additives for emission reduction [16,17] or octane number control [18], which is a fuel attribute that also relates to ignition control.

This line of work demonstrated that control of the chemical kinetics was the key to ignition control and already RCCI exhibits better ignition control than HCCI. This, of course, raises the question as to which are the appropriate additives that will be used for the purposes of ignition control. Fuel blends and cetane-number-affecting additives are certainly very intuitive initial choices. However, another, perhaps more systematic, way to determine such additives is to analyze the pertinent chemical dynamics with appropriate mathematical tools and identify species that have substantial impact on the dynamics through an algorithmic process.

In the past, such identifications were possible in the context of paper-and-pencil asymptotic analysis techniques, since the ignition-generating modes are related to the slow dynamics of the physical process [19,20]. However, when dealing with the large chemical kinetics mechanisms that are currently of interest, such techniques that rely strongly on the experience and intuition of the investigator are quite ineffective. Instead, the algorithmic methodologies for asymptotic analysis, which were developed in the late 80s and early 90s, are not hindered by the size or the complexity of the mechanisms [21–23]. These methodologies can identify the fast reactions that generate the fast dynamics and participate in the various equilibria that are thus established, as well as the slower reactions that generate the slow dynamics of the reacting system that characterize its evolution [24–32]. Such identifications are possible in the context of the fast/slow decomposition of the tangent space and of the role of each elementary reaction in such a decomposition [21–23]. The Computational Singular Perturbation (CSP) method provides an algorithm for such a decomposition and allows for the development of various tools that can identify the reactions that are responsible for the evolution of the system and for the generation of the dynamics that characterize this evolution [33,34].

In this paper, we utilize CSP tools in order to determine species that can affect the ignition delay of ethanol (EtOH)/air and di-methyl-ether (DME)/air mixtures. We focus on these two fuels not only because they have recently been utilized (EtOH) or proposed (DME) as possible renewable fuels, but also because they are isomers. As a result of them being isomers, the two fuels present very closely similar thermochemistry (heat release, adiabatic flame temperature). However, their autoignition is characterized by drastically different kinetics, as it has been shown recently [31]. Therefore, they are ideally suited in order to examine kinetic effects.

After determining the species with a substantial impact on the dynamics of the oxidation, we examine computationally the effect that their addition to the initial mixture would have on ignition delay. Through this process, we have been able to determine some simple combustion intermediates, which exist also as stable, relatively cheap chemicals (formaldehyde, acetaldehyde, hydrogen peroxide), and whose addition to the initial fuel can drastically affect and effectively control ignition delay.

## 2. Physical problem and CSP tools

The chemical kinetics mechanism that applies to the oxidation of both DME and EtOH consists of $N = 253$ species, $E = 6$ elements

(O, H, C, N, Ar and He) and $K = 1542$ elementary reactions [35]. Considering the forward and backward directions of the $K$ elementary reactions as separate unidirectional ones, the governing equations for the adiabatic autoignition of a homogeneous mixture at constant volume are:

$$\frac{d\mathbf{y}}{dt} = \frac{1}{\rho}\mathbf{W} \cdot \sum_{k=1}^{2K}\mathbf{S}_k R^k \tag{1}$$

$$\frac{dT}{dt} = \frac{1}{\rho c_v}(-\mathbf{h}_c \cdot \mathbf{W} + RT\mathbf{U}) \cdot \sum_{k=1}^{2K}\mathbf{S}_k R^k = \sum_{k=1}^{2K} v_k R^k \tag{2}$$

where $\mathbf{y}$ is the $N$-dimensional column vector of the species' mass fraction, $\mathbf{S}_k$ and $R^k$ represent the stoichiometric vector and reaction rate, respectively, of the $k$-th unidirectional reaction, $\rho$ 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, $\mathbf{U} = [1, 1, \ldots, 1]$ and $v_k = (-\mathbf{h}_c \cdot \mathbf{W} + RT\mathbf{U}) \cdot \mathbf{S}_k/(\rho c_v)$ [36,37].

In CSP form, Eqs. (1) and (2) are cast in the form:

$$\frac{d\mathbf{z}}{dt} = \mathbf{g}(\mathbf{z}) = \sum_{k=1}^{2K}\hat{\mathbf{S}}_k R^k = \sum_{n=1}^{N-E+1}\mathbf{a}_n f^n \tag{3}$$

where $\mathbf{z}$ is the $(N+1)$-dim. state column vector, defined as $\mathbf{z} = [\mathbf{y}, T]^T$, $\mathbf{a}_n$ is the $(N+1)$-dim. CSP column basis vector of the $n$-th mode and $f^n$ is the related amplitude $f^n = \mathbf{b}^n \cdot \mathbf{g}(\mathbf{z})$ and $\mathbf{b}^i \cdot \mathbf{a}_j = \delta^i_j$ [33,34]. The amplitudes $f^{N-E+2}$ to $f^{N+1}$ represent the conservation of the $E$ elements and they are by definition zero. When the $M$ fastest time scales of the system in Eq. (3) are exhausted, the system reduces to:

$$f^m \approx 0 \quad (m = 1, \ldots, M) \qquad \frac{d\mathbf{z}}{dt} \approx \sum_{n=M+1}^{N-E+1}\mathbf{a}_n f^n \tag{4}$$

The algebraic $M$-dimensional system $f^m \approx 0$ defines a low dimensional surface in tangent space, known as Slow Invariant Manifold (SIM), on which the solution evolves and the $(N+1)$-dimensional system of ODEs governs the slow evolution of the process on the SIM [21,23]. This system is free of the $M$ fast time scales ($\tau_1$ to $\tau_M$) and its dynamics are characterized by the fastest of the slow $(N - M - E + 1)$ time scales, when the solution evolves sufficiently far from the boundaries of the SIM [38,39].

The time scales of the system in Eq. (3) are approximated by the relation $\tau_n = |\lambda_n|^{-1}$ $(n = 1, \ldots, N - E + 1)$, where $\lambda_n$ is the $n$-th non-zero eigenvalue of the Jacobian $\mathbf{J}$ of $\mathbf{g}(\mathbf{z})$. When the real part of $\lambda_n$ is positive (negative), the related time scale $\tau_n$ 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), respectively, eigenvectors of $\mathbf{J}$. The $n$-th eigenvalue can be expressed as:

$$\lambda_n = \boldsymbol{\beta}^n \cdot \sum_{k=1}^{2K}grad\left(\hat{\mathbf{S}}_k R^k\right) \cdot \boldsymbol{\alpha}_n = c_1^n + \cdots + c_{2K}^n \tag{5}$$

since $\mathbf{J} = grad(\hat{\mathbf{S}}_1 R^1) + \cdots + grad(\hat{\mathbf{S}}_{2K} R^{2K})$ [30,24]. Considering the case where $\lambda_n$ is real (the extension to the case where some of the eigenvalues are complex pairs is straightforward [25]), the expression in Eq. (5) suggests the introduction of the *Time scale Participation Index* (TPI):

$$J_k^n = \frac{c_k^n}{|c_1^n| + \cdots + |c_{2K}^n|} \tag{6}$$

where $n = 1, \ldots, N - E + 1, k = 1, \ldots, 2K$ and by definition $\sum_{k=1}^{2K}|J_k^n| = 1$ [30,24,25]. $J_k^n$ measures the relative contribution of