The mechanism by which CH_2O and H_2O_2 additives affect the autoignition of CH_4/air mixtures

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***Abstract*— The case of the homogeneous autoignition of CH_4/air mixtures is considered and the effects of addition of the stable intermediates CH_2O and H_2O_2 in the initial fuel are explored. These two species are identified as those relating the most to the explosive mode that causes autoignition, throughout the largest part of the ignition delay. It is shown that the addition of small amounts of these species in the initial mixture can produce significant changes in the ignition characteristics.**

I. Introduction

Novel low temperature internal combustion engine concepts, like HCCI and RCCI, move towards designs that emphasize more strongly the control of the real time history of combustion through chemistry, in order to increase efficiency and reduce emissions [1]. Such concepts hold the promise of significantly improved efficiency and reduced emissions without the need for after treatment. Main obstacles in realizing the potential benefit from these concepts are the ability to optimize ignition and burning rate timing. The effectiveness of blending two or more fuels on phasing control was addressed in numerous experimental and numerical studies (see [1], [2] and [3] and the reference therein).

It becomes apparent that in view of the new engine technologies and fuels we need to understand how to identify and then integrate in the fuel the proper components in order to reach the optimal combustion behavior. To the best of our knowledge, all current attempts are based on a trial and error approach of trying different blends. In this work a methodology based on the tools provided by the Computational Singular Perturbation (CSP) algorithm is proposed to identify candidate additives in order to enhance the autoignition of a stoichiometric methane/air mixture. The analysis continues the work reported in Refs. [4] and [5].

The adiabatic autoignition of a homogeneous stoichiometric methane/air mixture is considered at constant volume. The chemical kinetics mechanism employed here is the v.3.0 GRI mechanism, consisting of N = 53 species and K = 325 elementary reactions. The reactions and species that promote or oppose autoignition will be identified using CSP tools; the time scale participation Index (TPI) and the Pointer (Po), which identify the reactions and variables related to a particular mode. This information will then form the basis for the selection, among the various intermediates, of the additives that can control effectively the ignition delay.

II. Results

The reactions that promote or oppose the autoignition of a CH_4/air mixture in the case of $p_0 = 4$ MPa, $T_0 = 900$K, $\phi = 1$ are listed in Table I. These reactions were identified with TPI as those being responsible the most for the generation of the fastest explosive time scale, say $\tau_{e,f}$, that characterizes the dynamics of the system and is among the fastest of the reduced model that applies in this case.

TABLE I
The reactions exhibiting the largest TPIs for the fast explosive time scale $\tau_{e,f}$.

(32f)	$O_2 + CH_2O \rightarrow HO_2 + HCO$
(38f)	$H + O2 \rightarrow O + OH$
(52f)	$H + CH_3(+M) \rightarrow CH_4(+M)$
(84)	$OH + H_2 \leftrightarrow H + H_2O$
(85b)	$2OH(+M) \leftarrow H_2O_2(+M)$
(89)	$OH + H_2O_2 \leftrightarrow HO_2 + H_2O$
(99f)	$OH + CO \rightarrow H + CO_2$
(115f)	$2HO_2 \rightarrow O_2 + H_2O_2$
(116f)	$2HO_2 \rightarrow O_2 + H_2O_2$
(119f)	$HO_2 + CH_3 \rightarrow OH + CH_3O$
(121f)	$HO_2 + CH_2O \rightarrow HCO + H_2O_2$
(155f)	$CH_3 + O_2 \rightarrow O + CH_3O$
(156f)	$CH_3 + O_2 \rightarrow OH + CH_2O$
(157)	$CH_3 + H_2O_2 \leftrightarrow HO_2 + CH_4$
(158f)	$2CH_3(+M) \rightarrow C_2H_6(+M)$
(161f)	$CH_3 + CH_2O \rightarrow HCO + CH_4$
(287f)	$OH + HO_2 \rightarrow O_2 + H_2O$

The set of reactions in Table I was constructed by identifying the reactions contributing the most to the generation of $\tau_{e,f}$ at various points along the ignition delay time t_{ign}=0.1632 s. The reactions contributing the most to $\tau_{e,f}$ at eight points between $t = 0$ and $t = t_{ign}$ are listed in Table II, along with the variables related the most to the corresponding fast explosive mode.

It is shown in Table II that the species relating the longest to the explosive mode are CH_2O and H_2O_2. When using these species as additives to methane, Table III shows that they produce by far the largest change in the value of

TABLE II

THE LARGEST TPI AND POINTER INDICES FOR THE FAST EXPLOSIVE MODE, IN THE CASE $p_0 = 4$ MPA, $T_0 = 900$K, $\phi = 1$; NUMBERS IN PARENTHESIS DENOTE POWER OF TEN. REACTIONS INVOLVING H/O CHEMISTRY ARE INDICATED BY BOLD NUMBERS. t_{ign}=1.632(-1) S.

t_1=0.000(0)	t_2=2.023(-3)	t_3=5.002(-2)	t_4=1.0001(-1)	t_5=1.5003(-1)	t_6=1.631990(-1)	t_7=1.631994(-1)	t_8=1.631995(-1)
$\tau_{e,f}$=3.11(-3)	$\tau_{e,f}$=2.59(-2)	$\tau_{e,f}$=3.76(-2)	$\tau_{e,f}$=2.73(-2)	$\tau_{e,f}$=8.62(-3)	$\tau_{e,f}$=5.49(-7)	$\tau_{e,f}$=2.15(-7)	$\tau_{e,f}$=4.48(-7)
TPI							
158f : -0.47	158f : -0.37	119f : +0.21	119f : +0.21	119f : +0.23	**38**f : +0.14	**38**f : +0.19	**38**f : +0.18
155f : +0.33	32f : +0.19	32f : +0.18	158f : -0.13	**85b** : +0.14	52f : -0.08	**84**f : +0.08	99f : +0.12
157b : +0.07	156f : +0.15	158f : -0.17	32f : +0.12	121f : +0.12	**89**b : +0.07	**287**f : -0.07	**287**f : -0.07
85b : +0.05	155f : +0.12	161f : +0.07	**116**f : -0.08	**116**f : -0.12	**287**f : -0.05	**89**b : +0.07	**84**b : -0.06
32f : +0.04	119f : +0.05	156f : +0.06	161f : +0.08	158f : -0.09	**84**f : +0.05	**84**b : -0.06	**84**f : +0.06
Po							
CH_3 : +0.70	CH_2O : +0.76	CH_2O : +0.85	CH_2O : +0.77	H_2O_2 : +0.38	T : +0.95	T : +1.49	T : +3.52
HO_2 : +0.13	H_2O_2 : +0.15	H_2O_2 : +0.10	H_2O_2 : +0.16	CH_2O : +0.36	O_2 : - 0.15	O_2 : - 0.42	O_2 : - 1.08
H_2O_2 : +0.09	HO_2 : +0.06	HO_2 : +0.03	T : +0.04	T : +0.24	CH_4 : +0.11	HO : +0.13	CO_2 : - 0.87

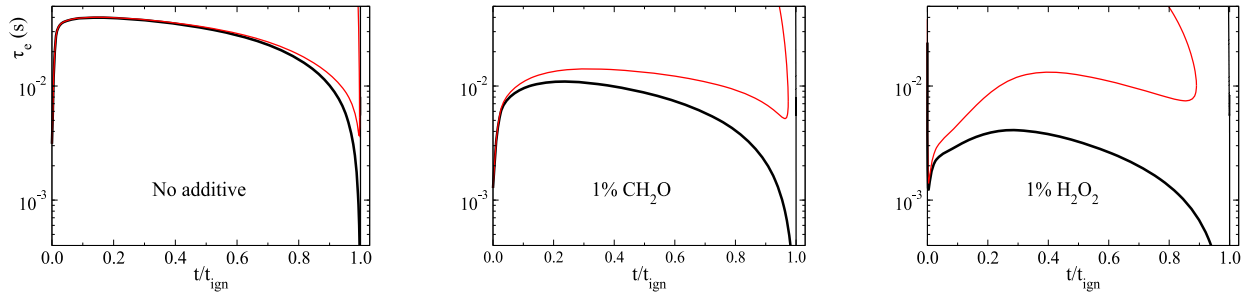

Fig. 1. The evolution of $\tau_{e,f}$ in the cases of no additives, 1% CH_2O and 1% H_2O_2; $p_0 = 4$ MPa, $T_0 = 900$ K and $\phi = 1$. Black lines denote the time scales computed on the basis of the species and energy equations, while red lines denote the time scales computed on the basis of the species equation.

TABLE III

THE % CHANGE OF IGNITION DELAY τ_{ign} IN THE CASE WHERE THE NUMBER OF MOLES OF THE FUEL CONSIST BY 99% OF METHANE AND BY 1% OF A STABLE INTERMEDIATE, RELATIVE TO τ_{ign} IN THE CASE OF THE PURE FUEL.

CH_2O	-84.9 %	H_2O_2	-95.4 %	H_2	-40.3 %
HCCOH	0.4 %	C_3H_8	-0.7 %	C_2H_6	-33.8 %
C_2H_4	-35.6 %	C_2H_2	-4.1 %		

t_{ign}. When acting as additives, other stable intermediates produced significantly smaller changes to t_{ign}.

In order to investigate the cause of this significant influence of CH_2O and H_2O_2, when present by a small amount in the initial mixture, the fast explosive time scale $\tau_{e,f}$ was computed when taking into account the temperature equation and when ignoring it. In the *chemical runaway* regime these two time scales must be close to each other, while in the *thermal runaway* regime they deviate considerably.

The results shown in Fig. 1 demonstrate that the presence of CH_2O and H_2O_2 in the initial mixture reduces considerably the *chemical runaway* regime. As a result, in the presence of the two additives the process enters the *thermal runaway* regime faster, so that the steep temperature increase that is generated there [5], [6] causes the mixture to ignite faster. It can be shown that the addition of CH_2O and H_2O_2 activates specific reactions involving these species as reactants from the beginning of the autoignition process, which were not as influential towards the generation of $\tau_{e,f}$ in the case were these two species were not present in the initial mixture.

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REFERENCES

[1] F.L. Dryer, "Chemical kinetic and combustion characteristics of transportation fuels", *Proc. Combust. Inst.* 35 (2015) 117144.

[2] T.M. Foong, K.J. Morganti, M.J. Brear, G. da Silva, Y. Yang, F.L. Dryer, "The octane numbers of ethanol blended with gasoline and its surrogates", *Fuel*, 115 (2014) 727739.

[3] A. Ahmed, G. Goteng, V.S.B. Shankar, K. Al-Qurashi, W.L. Roberts, S.M. Sarathy, "A computational methodology for formulating gasoline surrogate fuels with accurate physical and chemical kinetic properties", *Fuel*, 143 (2015) 290300.

[4] D.J. Diamantis, D.C. Kyritsis, D.A. Goussis, "The reactions favoring or opposing the development of explosive modes: autoignition of a homogeneous methane/air mixture", *Proc. Combust. Inst.* 35 (2015) 267-274.

[5] D.J. Diamantis, E. Mastorakos, D.A. Goussis, "H_2/air autoignition: the nature and interaction of the developing explosive modes", *Combust. Theory and Model.* in press.

[6] T. Lu, C.S. Yoo, J.H. Chen, C.K. Law, "Three-dimensional direct numerical simulation of a turbulent lifted hydrogen jet flame in heated coflow: a chemical explosive mode analysis", *J. of Fluid Mech.* 652 (2010) 4564.