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Some aspects of combustion chemistry of C1–C2 oxygenated fuels in low pressure premixed flames

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Abstract

The increasing utilization of renewable fuels in the transportation and industrial sectors has sparked an interest in understanding the combustion of relevant major fuel components. Among them, smaller, oxygenated compounds, are of particular importance, both as neat fuels and as potential blending agents in engines operating on practical fuels. Additionally, oxygenated exhaust species, e.g. small aldehydes, are harmful and are expected to be regulated by future emission standards. The assessment of the effect of specific fuel components on overall engine efficiency and performance, as well as on pollutants formation, needs to be tackled through a detailed kinetics approach that inherently allows such a correlation. In the present work, a single, in-house developed, detailed chemical kinetic mechanism is utilized in order to model and analyze five stoichiometric or near stoichiometric low-pressure laminar premixed flames of C1–C2 oxygenated fuels; flames of the two smallest aldehydes (formaldehyde and acetaldehyde) and the two smallest alcohols (methanol and ethanol) are considered. The mechanism is shown to satisfactorily reproduce fuel decay as well as major and intermediate species profiles. Reaction path analysis is extensively utilized in order to scrutinize the controlling elementary steps. Parts of the mechanism are identified for further model improvement, based on critical evaluation of available specific rate constants. Early branching ratios and reactions between the major carbonyl or alkoxy products with oxygen carriers, and in particular reactions with O_2, appear to be pivotal for the overall oxidation process.

Keywords: Laminar premixed flames; Alcohols; Aldehydes; Non-regulated Pollutants; Detailed chemical kinetics

1. Introduction

The quest for clean and efficient energy utilization has revealed the need for integrated design of fuels and energy conversion processes, aiming towards optimized performance and reduced emissions (e.g. [1,2]). In both mobile and stationary applications, there is a growing trend towards chemically controlled combustion, such as the HCCI/PCCI/RCCI modes for efficient and fuel flexible ICE operation (e.g. [3]) and the FLOX/MILD burner mode ([4,5]). The increasing utilization of alternative renewable fuels, including

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smaller fuels with possible oxygenated content, such as syngas and small alcohols, requires a detailed mapping of their respective chemistry, particularly at conditions pertinent to the above advanced combustion modes, e.g. [7].

The combustion of novel bio-fuels in practical engines may lead to significant emissions of gaseous pollutants such as C1–C2 aldehydes, due to the oxygen content of the fuel and the combustion mode. Although such species are not currently regulated, there are indications [8,9] that limits may be imposed in the not so distant future, mainly due to their adverse health effects [10]. However, in situ quantitative measurements of such species are relatively difficult to perform, and as a result they are currently mostly reported at the exhaust, thus providing limited kinetic information. Further, observed trends in exhaust levels of typical species are not generally consistent and are largely dependent on operating conditions.

Assessing the effect of oxygenated fuel components on the combustion process, including pollutants formation, needs to be tackled through a detailed kinetics approach. Several relevant reaction mechanisms are available in the literature (e.g. [6,11]). However, recent significant advances in thermo-chemical and kinetic parameters assessment with respect to C1–C2 combustion chemistry (e.g. [12]), suggest a critical re-evaluation of existing mechanistic approaches. Additionally, the increasing wealth of experimental speciation data from fundamental configurations, and especially premixed flames (e.g. [13]), and the numerous theoretical investigations and experimental campaigns at engine level utilizing neat bio-fuels or blends of practical and oxygenated fuels, necessitate the development of a flexible combustion chemistry model able to describe the oxidation of a range of fuels for a range of operating conditions (see also relevant reviews, as e.g. [14,15]).

In the present work, a single, comprehensive detailed chemical kinetic mechanism [16], is utilized in order to model and analyze five stoichiometric or near stoichiometric low-pressure laminar premixed flames of C1–C2 oxygenated fuels, see Table 1. At first, each flame is considered separately and both major fuel consumption and product formation pathways are discussed and evaluated. The analysis focuses on the mechanism development procedure, primarily based on the critical evaluation of literature kinetic and thermochemical data. In the last part of the paper general conclusions on the combustion chemistry of small oxygenates are presented.

2. Development of a flame database and numerical methodology

Flames of the two smallest aldehydes, formaldehyde and acetaldehyde, and the two smallest alcohols, methanol and ethanol, have been considered, see Table 1. Both formaldehyde and acetaldehyde are key intermediates in the combustion of higher hydrocarbons. Formaldehyde is also an important intermediate species in the combustion of methanol, while both aldehydes have a prominent role in the oxidation process of lean, stoichiometric and rich ethanol mixtures. A comprehensive mechanism for the combustion of small and medium-sized hydrocarbons, as appeared in [16], has been used as the starting point. The implemented mechanism has been extensively validated against experimental speciation data from counterflow and premixed flames, including laminar flame speeds, shock tubes, including ignition delay times, and perfectly stirred and plug-flow reactors, all under a wide range of temperatures, pressures, and stoichiometries [22–25]. The current version of the mechanism consists of 142 species and 834 reactions (see Supplementary material).

The experimentally determined temperature profiles have been imposed to calculations, so that heat losses to the burner are explicitly taken into account. The multi-component diffusion model was mostly used, and grid adaptation parameters have been chosen so as to insure high grid resolution and grid-independent solutions. Thermal diffusivity effect has been taken into account. All computations have been performed using the CHEMKIN software [27]. More information about the numerical methodology can be found in [16,26].

3. Formaldehyde chemistry

The mechanism accurately reproduce fuel decay, major products and key radical profiles in

Table 1
The premixed flames computed in the present work.

Flame	Fuel	ϕ	Fuel	O_2	Ar	p (mbar)	u_o (cm/s)*	Refs.
FF1	CH_2O	1.09	0.177	0.163	0.66	30	80 (300 K)	[17]
FA1	CH_3CHO	1.00	0.075	0.187	0.738	50	44.5 (298 K)	[18]
FM1	CH_3OH	0.89	0.199	0.337	0.464	53.3	43 (298 K)	[19]
FE1	C_2H_5OH	1.00	0.069	0.206	0.725	50	55.7 (298 K)	[20]
FE2	C_2H_5OH	1.00	0.1875	0.5625	0.25	50	50 (298 K)	[21]

* Initial velocity (and its reference temperature) at burner tip as given in the respective original publications.