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Experimental and Modeling Study of Premixed Methyl Pentanoate Flames Stabilized at Atmospheric and Low-Pressure Conditions.

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Abstract

Detailed chemical structures of stoichiometric and rich premixed laminar flames of methyl pentanoate were investigated over a flat burner at 20 torr and at 1 atm. Molecular beam mass spectrometry was used with tunable synchrotron vacuum ultraviolet (VUV) photoionization for low pressure flames, and soft electron-impact ionization was used for atmospheric pressure flames. Mole fraction profiles of temperatures and stable and intermediate species were measured in the flames. Two detailed mechanism were implemented, one of which have not been published earlier. Both mechanisms have shown a good agreement with experiments for the most species, but however for a several compounds considerable discrepancies between calculated and measured mole fractions of the species were observed. Analysis of the reaction pathways has shown some noticeable differences between two mechanisms and the need of a significant improvement of a both mechanism to achieve a better agreement with an experimental results.

1. Introduction

Search for renewable sources of energy aimed at reducing oil consumption in energy production and transport is causing increasing interest for different oxygenated fuels. One of the most promising types of these fuels is biodiesel based on methyl esters. It is produced from plant oils and animal fats by transesterification, and thus consists of a mix of several methyl esters with 15-18 carbon atoms in the alkyl chain. The actual composition of biodiesel can vary depending on the source it is made of. It has been demonstrated in different studies that the use of biodiesel fuels can reduce generation of soot, CO and NO_x in internal combustion engines [1]. Therefore, for combustion parameters to be evaluated in different systems, it is crucial to know the kinetic mechanisms of combustion for all the all biodiesel components.

However, the high molecular weight and the complex structure of the biodiesel components lead to a huge diversity of its decomposition products, which are very difficult to analyze, and requires development of extended detailed kinetic mechanisms. Some progress in this area has been achieved [2], but the mechanisms proposed still require additional experimental data to be validated. Thus, most research works in this area focus on the chemistry of lighter esters, such as methyl butanoate, methyl decanoate and some others, with subsequent extrapolations of the kinetic schemes on larger molecules.

Although there are a lot of papers devoted to methyl esters, only a few of them study flame systems. In particular, combustion of methyl pentanoate (C₆H₁₂O₂, MPe) had not been studied before except for oxidation studies in a jet-stirred reactor [3] and some numerical simulations [4]. In this work, structure of four



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MPE flames stabilized at atmospheric and low (20 Torr) pressures has been studied with molecular-beam mass-spectrometry (MBMS) experimental technique and numerical simulations. For these simulations two different detailed kinetic mechanisms were implemented. One of them was proposed earlier [3], and the other one was prepared and validated on a new obtained experimental data by authors of this work.

2. Approach

The structure of four premixed MPE/O₂/Ar flames with equivalence ratios $\phi = 1.0$ and $\phi = 1.5$ was studied in this work. Low pressure flames were studied by a time-of-flight mass spectrometer with a molecular beam sampling system and photoionization by tunable VUV synchrotron radiation located at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory [5]. These flames were stabilized at pressure of 2.67 kPa (20 Torr) on a 6-cm in diameter McKenna burner. The following flame conditions were selected (in mole fractions): 0.057/0.443/0.5 for a stoichiometric flame and 0.079/0.421/0.5 for a fuel rich flame. The linear velocity of the fresh mixture on the burner surface was 72 cm/s for both flames.

Flames stabilized at atmospheric pressure conditions were studied by MBMS setup with a quadrupole mass-spectrometer and soft electron-impact ionization located in Novosibirsk [6]. A flat burner 16 mm in diameter with a surface maintained at 90°C was used in these experiments. Flame composition for a stoichiometric and a fuel rich flames were 0.023/0.177/0.8 and 0.047/0.253/0.7 correspondingly, with the linear velocity of the fresh mixture on the burner surface of 12.43 cm/s and 7.58 cm/s.

In atmospheric pressure experiments samples taken from flames at several distances were also analyzed with a gas chromatography/mass-spectrometry (GC/MS) system (Agilent HP6890/5973N). It allowed to indentify the main products of MPE decomposition and their isomers using mass spectra from the standard database.

Temperature measurements in low pressure flames were performed by OH-LIF spectroscopy. In atmospheric flames temperature were measured by Pt/Pt+10%Rh thermocouple welded from wire 0.02 mm in diameter, coated with a thin layer of SiO₂ to prevent catalytic recombination of radicals on the thermocouple surface. As a result, the thermocouple had a diameter of 0.03 mm and a shoulder length of about 3 mm, ensuring negligible heat losses to the cold ends.

Numerical simulations were performed with a PREMIX code from the CHEMKIN package. The first mechanism were developed and validated by Dayma et al. [3] and based on their experimental data obtained in a jet-stirred reactor. It contained 215 species and 1630 reactions. The other mechanism was recently developed for small esters combustion and included all methyl esters up to methyl hexanoate with an updated thermochemistry data for these compounds. It should be noted that low temperature oxidation reactions were excluded from the last mechanism to increase performance. After it this mechanism included 404 species and 2561 reactions.

3. Results and discussion

Mole fraction profiles of all major species (MPE, CO, CO₂, H₂O, O₂) were obtained in all 4 studied flames. Fig. 1 presents experimental results and results of numerical modeling with both mechanisms for two stoichiometric flames under study. As it can be seen from the image, both mechanisms

agree very well with the results of MBMS experiments both in absolute values and in flame width. Small discrepancies can be addressed to a calibration procedure and to the experimental error.

A large amount of intermediate species also were measured in these flames.

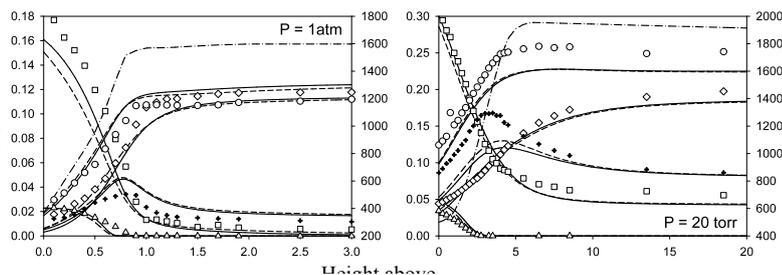


Fig. 1. Mole fraction profiles of major species in stoichiometric MPE flames. Squares – O₂, circles – H₂O, diamonds – CO₂, pluses – CO, triangles – MPE,

Hydrogen,
methyl
radical,
methane,
acetylene,
ethylene,
propyne,
butadiene,
1-butene,
methyl
acrylate,

methyl propanoate and methyl-3-butenolate mole fraction profiles were obtained in both stoichiometric and low-pressure flames. And because of a higher resolution a several species which includes: formaldehyde, methanol, ketene, propene, acetaldehyde, propane, vinylacetylene, acetone and propylenoxide were also measured but only in low-pressure conditions. Some of these profiles presented on the Fig. 2. For the most species a very good agreement between both models and experiment was observed, with a noticeable disagreement for only a few measured species. Figure 2 also shows that there are several important differences between the two implemented combustion mechanisms. These differences are more evident for a heavy species which are a direct products of a MPE oxidation in flame.

Analysis of a reaction pathways showed that one of the most important factors are differences in thermochemistry data for a radicals produced directly from MPE. By changing the balance between these radicals mechanism leads to a different distribution between heavy intermediates in flames. These important observations will lead to a further mechanism development.

4. Conclusions

An experimental data on structure of premixed flames of methyl pentanoate stabilized at two different pressures are compared to new chemical kinetic modeling results in this work. Two detailed mechanism were implemented, one of which have not been published earlier. Both mechanisms have shown a good agreement with experiments for the most species, but however for a several compounds considerable discrepancies between calculated and measured mole fractions of the species were observed. Analysis of the reaction pathways has shown some noticeable differences between two mechanisms and the need of a significant improvement of a both mechanism to achieve a better agreement with an experimental results.

5. Acknowledgements

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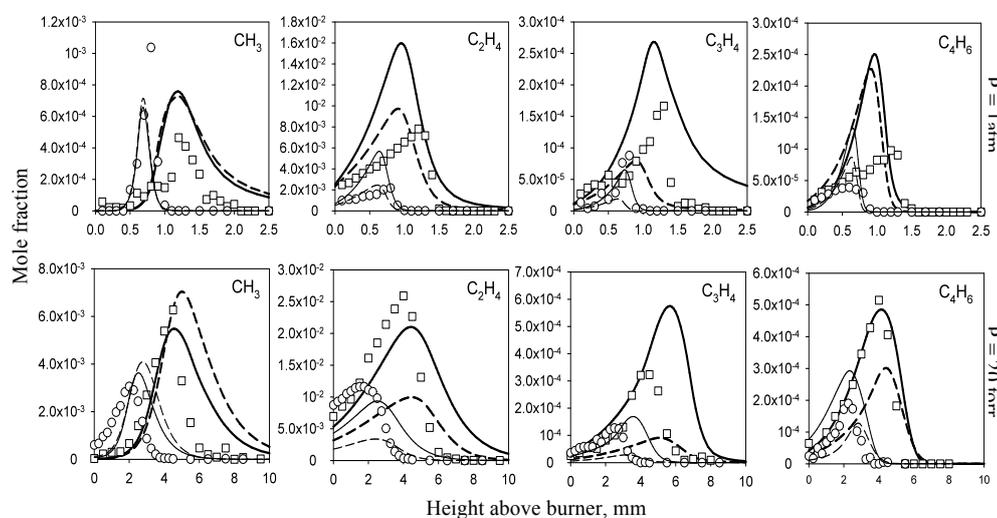


Fig. 2. Mole fraction profiles of several intermediate species in studied flames. Symbols – experiment, curves – modeling; circles and thin lines – stoichiometric flames, squares and thick lines – fuel-rich flames; solid lines – modeling with mechanism [3], dashed lines – modeling with new mechanism; top diagrams – atmospheric