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Propagation of sub-atmospheric methyl formate flames

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ABSTRACT

Laminar flame speeds of methyl formate/air mixtures were measured at sub-atmospheric pressures for which limited data exist. The experiments were carried out in the counterflow configuration at an unburned mixture temperature of 333 K. The flow velocities were measured using particle image velocimetry. Particle phase slip correction was applied to low-pressure data sets for which the density disparity between the flow tracers and the gaseous phase is notable. The data were modeled using two recently developed kinetic models of methyl formate oxidation, and significant disagreements were realized at all pressures especially under fuel-rich conditions. Additionally, the computed species profiles of CO and CO_2 in the burner-stabilized flame configuration using the two models were found to differ significantly. Reaction path analysis revealed that the kinetics of CH_2OCHO that is produced directly from the fuel affects the overall reactivity, and the attendant rate constants differ between the two models. The variation of laminar flame speed with pressure revealed also a different behavior between experiments and simulations. Further insight into the sources causing the observed discrepancies were investigated and it was determined that reactions involving formyl radical, methanol, and formaldehyde could also be responsible for the reduction in reactivity specifically under fuel-rich conditions.

1. Introduction

Biodiesel fuels are manufactured by the esterification of renewable oils, fats, and fatty acids [1]. They generally operate well in diesel engines, with another attractive feature being that the oxygen atoms imbedded within the biodiesel fuel molecule tend to reduce soot emissions [2]. However, the kinetics of biodiesels composed of large alkyl esters is not yet well established. Similarly to hydrocarbons, it is essential that the kinetics of smaller molecular weight alkyl esters is studied first so that the foundation is established over which the chemistry of the heavier esters could be built on.

While high pressures are relevant to ground transportation, propulsion, and power-production applications [3], accurate model prediction at atmospheric pressure is essential for two reasons. First, the experimental data at atmospheric conditions are characterized in general by notably lower uncertainty compared to engine-relevant pressures [4]. Second, at atmospheric and sub-atmospheric pressures for that matter, the effects of three-body reactions are minimized and thus the rates of important two-body reactions can be better validated.

Methyl formate (MF) is the smallest alkyl ester and its combustion properties have been investigated experimentally in relatively few studies [5–8]. Nevertheless, the lack of an extensive set of reliable data makes it difficult to validate kinetic models with certainty. For example, MF flame kinetics has been established based on molecular beam mass spectrometry (MBMS) speciation data in low-pressure flames [5]. The technique involves intrusion of a sampling probe into a low-pressure flame, which allows flame structure measurements with satisfactory spatial resolution. However, recent studies [9–11] have shown that probe effects can be substantial due to heat loss and aerodynamic effects, and as a result the measured flame structure deviates notably compared to that of a one-dimensional unperturbed flame that is the key assumption for modeling the data.

While the model of Westbrook et al. [5] has been shown to provide generally satisfactory agreements with speciation data obtained in $p = 40$ mbar laminar premixed MF/O_2/Ar flames, in a recent study of $p = 1$ atm MF/air flames, Wang et al. [6] showed that the experimental laminar flame speeds, S_u, disagree with the predicted values using the kinetic model of Ref. [5] by almost 10–15 cm/s under fuel-rich conditions. Specifically, it has been reported [5] that the measured profiles of major species such as carbon monoxide, carbon dioxide, water, and hydrogen agree reasonably well with the simulation results, while other measured profiles such as C_2H_6, C_2H_2, and CH_2O could not be reproduced well by the model. On the other hand, comparisons of the S_u data of Wang et al. [6] against predictions obtained using the more recent methyl ester oxidation model of Diévart et al. [12] showed a

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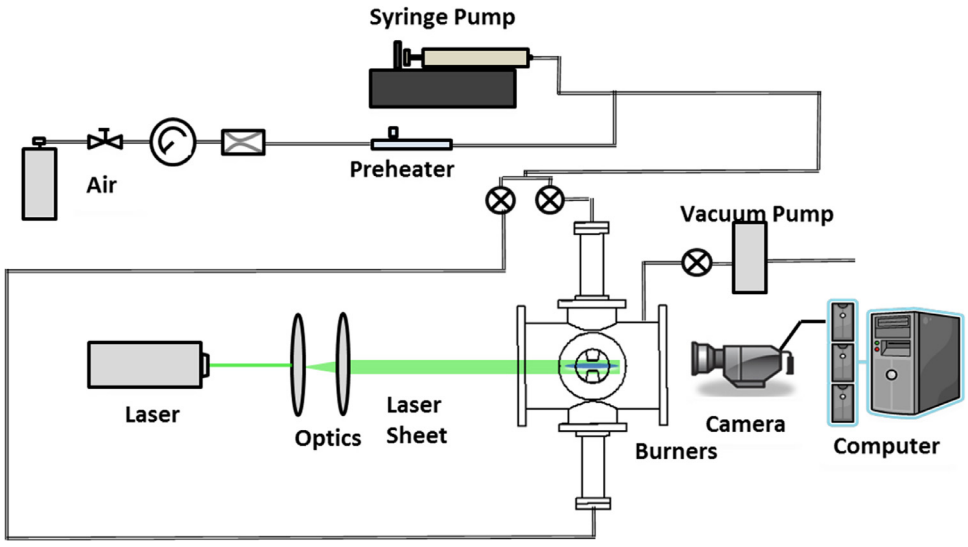

Fig. 1. Schematic of the counterflow twin-flame experimental system.

close agreement for fuel lean conditions but the data are overpredicted by about 5–7 cm/s under fuel-rich conditions. These discrepancies observed in low pressure speciation and atmospheric flame propagation measurements raise the questions of whether there is a kinetic knowledge gap between $p = 40$ mbar and $p = 1$ atm, and whether systematic experimental error was properly accounted for in the reported speciation data [5].

Based on the aforementioned findings, it is apparent that S_u data are needed at pressures that are notably less than 1 atm in order to provide additional constraints to model validation and further insight into the observed discrepancies. However, measuring flow velocities at low pressures using flow tracers and laser-based approaches such as laser Doppler velocimetry (LDV) or particle image velocimetry (PIV) introduces additional complexity due to the potential velocity slip between the particle and gas phases. For example, Egolfopoulos and Campbell [13] have shown that the gas and particle phase velocities in opposed-jet configuration can substantially differ from each other for "heavy" particles in the presence of large temperature gradients and large strain rates. This discrepancy is expected to be more profound at lower pressures as the density disparity between the two phases increases.

Other than the validation of speciation studies at mbar-level pressures, there has been no practical motivation to perform any additional flame experiments at low pressures. In particular, in most published studies, the goal is to measure S_u at pressures that are as high as possible given the relevance of such data to engine conditions. As a result, S_u data at sub-atmospheric conditions are scarce. A survey of nearly 120 papers published in the major combustion journals on experimental determination of S_u reveals that ~65% have been carried out at $p = 1$ atm, ~27% for $p > 1$ atm, and only ~8% at $p < 1$ atm.

Zhu et al. [14] measured S_u of methane/air mixtures at 0.25 atm in the counterflow configuration. Egolfopoulos and co-workers [14–17] measured S_u of C_1- and C_2-hydrocarbon flames at 0.25 atm and H_2 flames at 0.2 atm. Smallbone et al. [18] carried out S_u measurements of *n*-heptane flames at 0.5 atm in the counterflow configuration. Few $p < 1$ atm S_u measurements have been conducted in spherically expanding flames (e.g., [19–21]). Measurements of S_u at $p < 1$ atm have been made also in other configurations (e.g., [22,23]).

In view of these considerations, the main goal of the present study was to investigate experimentally and computationally flame propagation of MF/air mixture at sub-atmospheric pressures, and provide insight into the controlling mechanisms. As mentioned earlier, under such conditions three-body reactions and related chemistry with uncertain kinetics, e.g. hydroperoxyl radical (HO_2), are expected not to be important so that the rates of two-body reactions can be validated with confidence.

2. Experimental approach

Measurements were performed in the counterflow twin-flame configuration [14–17]. The burner assembly was installed within a pressure chamber capable of operating between 0.05 and 5 atm. Measurements were performed for equivalence ratios, ϕ, between 0.9 and 1.5. Liquid MF (97+% purity; Alfa Aesar) was vaporized, and then mixed with air (e.g., [6]). The schematic of the counterflow twin-flame experimental system is shown in Fig. 1.

PIV was used to measure particle velocities. A double pulsed ND:YAG laser and a high performance 12 bit CCD camera with 1392×1024 pixels of resolution were used to acquire PIV images. Silicone oil for high temperature system (Alfa Aesar, CAS No. 68083-14-7) is used as flow tracers as it had better solubility in fuel than other types. Silicone oil was less than 1.5% of the total volume of the fuel and thus has negligible effect on the overall reactivity. Mixed silicone oil and fuel was injected into a high-efficiency nebulizer (Meinhard TR-50-A3) using a high-precision syringe pump. The minimum axial velocity along the system centerline just upstream of the flame was defined as reference flame speed, $S_{u,ref}$, and the maximum absolute value of the axial velocity gradient in the hydrodynamic zone was defined as the strain rate, K [14–17]. As K was varied its effect on $S_{u,ref}$ was recorded, and S_u was determined through a computationally-assisted extrapolation methodology to be discussed in the following section.

The experiments were conducted for $0.1 \le p \le 1.0$ atm and an unburned mixture temperature $T_u = 333$ (± 2) K. A single stage, rotary vane vacuum pump (Sogevac SV 40B) was used in order to keep the chamber pressure at a desired condition. In order to increase flame stability at lower pressures, burners with larger diameters, D, were used, and with burner separation distance $L = D$ for all experiments. At $p = 1.0$ atm burners with $L = D = 14$ mm were used, while at $0.2 \le p \le 0.5$ atm and at $p = 0.1$ atm, $L = D = 21$ mm and $L = D = 28$ mm were used respectively. The 1σ standard deviations in S_u are indicated with uncertainty bars in all relevant figures. Uncertainty in ϕ was determined to be no larger than 0.5%.