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Laminar burning velocities of methylcyclohexane + air flames at room and elevated temperatures: A comparative study

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Laminar burning velocities of methylcyclohexane + air flames were determined using the heat flux method at atmospheric pressure and initial temperatures of 298–400 K. The measurements were performed on two experimental setups at Lund University and Samara National Research University. Our results obtained at the same initial temperatures are in good agreement. Consistency of the measurements performed at different temperatures was tested employing analysis of the temperature dependence of the burning velocities. This analysis revealed increased scatter in the burning velocity data at some equivalence ratios which may be attributed to the differences in the design of the burners used. New measurements were also compared to available literature data. Reasonably good agreement with the data of Kumar and Sung (2010) was observed at 400 K, with significantly higher burning velocities at the maximum at 353 K as compared to other studies from the literature. Predictions of two detailed reaction mechanisms developed for jet fuels – PoliMi and JetSurF 2.0 were compared with the present generally consistent measurements. The two kinetic models disagreed with each other, with the experimental data being located in between the model predictions. Sensitivity analysis revealed that behavior of the models is largely defined by C_0–C_2 chemistry. Comparison of the model predictions with the burning velocities of ethylene and methane showed the same trends in over- and under-predictions as for methylcyclohexane + air flames.

1. Introduction

Aviation kerosene or jet fuel is a complex mixture of different classes of hydrocarbons with the major contributors being normal alkanes, branched chain paraffins (iso-alkanes), aromatic molecules and cyclic paraffins, cycloalkanes [1]. Formulation of the proper surrogate fuels reproducing practical (physical) and combustion characteristics of kerosene requires, therefore, detailed understanding of the combustion chemistry of each of these classes [2,3]. The laminar burning velocity, one of the most important characteristics of combustible mixtures, has been recently investigated in our flame studies of n-heptane [4,5] and n-decane [6] representing n-alkanes, of iso-octane [4,5], of aromatic benzene [7] and toluene [4].

Cycloalkanes possess unique combustion features important for oxidation of real fuels [8,9] such as low reactivity in low temperature oxidation as compared to n-alkanes. Methylcyclohexane, MCH, is one of the simplest representatives of the class, and many previous studies proposed methylcyclohexane as a component of surrogate blends for aviation or engine fuels, e.g. [9–17]. High-temperature conversion of methylcyclohexane was investigated by several research groups. Early studies of MCH pyrolysis were focused on its thermal stability [18] as it was considered as cooling agent of supersonic vehicles through endothermic decomposition [19]. Therefore overall methylcyclohexane decomposition rates and yield of major products were determined in a turbulent flow reactor [19]. The major intermediates of high-temperature (1050–1200 K) MCH pyrolysis were ethylene, 1,3 butadiene, methane and propene. Methylcyclohexane and ethylene time histories recorded in Stanford shock tube [20] confirmed C_2H_4 as a major product at high pressures around 20 atm from 1000 to 1500 K. Very low pressure pyrolysis of MCH yielded rate constant of primary reaction channel of ring opening [21]. Detailed study of the methylcyclohexane decomposition products at 30, 150 and 760 Torr and species concentrations in a low-pressure flame [22] was aimed at and contributed to the development of detailed kinetic models.

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Oxidation of MCH in a flow reactor at low temperatures below 673 K [23] revealed formation of aldehydes and ketones. Zeppieri et al. noted that at high temperatures oxidation of MCH proceeds faster than pyrolysis, yet major intermediates were found the same in both cases [19]. OH time-histories during oxidation of methylcyclohexane in a shock tube [24] were recorded to validate several detailed kinetic models discussed below.

Earlier study of MCH oxidation in an engine [25] revealed significant quantities of benzene and 1,3 butadiene in the exhaust. More recently, Yang and Boehman [26] measured products of low to intermediate temperature oxidation of methylcyclohexane in a motored engine and found that cyclohexane shows a stronger negative temperature coefficient (NTC) behavior than MCH. These results were further analyzed to elucidate important isomerization and other key reactions affecting NTC behavior [8,27].

Ignition delay measurements were performed in rapid compression machines by Tanaka et al. [28], Pitz et al. [29], Mittal and Sung [30], and Weber et al. [31]. Pitz et al. [29] covered temperatures of 700–1020 K and developed a detailed reaction scheme for methylcyclohexane oxidation taking the high-temperature part from an earlier shock-tube study of Orme et al. [32]. Mittal and Sung noted “substantial quantitative discrepancy” while using the model of Pitz et al. [29] for their conditions. Weber et al. [31] presented new ignition data in RCM at 50 bars and an updated version of the model of Pitz et al. [29] with cyclohexane sub-mechanism from Silke et al. [33]. The model [31] was validated against the new and previous ignition data [30,34,35], and an improvement over [29] was observed.

Several studies of MCH ignition in shock tubes were also performed for development and improvement of kinetic models [32,34,36,37]. Vanderover and Oehlschlaeger [34] and Vasu et al. [35] covered wide temperature range (795–1560 K) and extended the pressure range of the early measurements of Hawthorn and Nixon [38] up to 50–69.5 atm. Vanderover and Oehlschlaeger [34] suggested to increase rate constants for H-abstraction from methylcyclohexane to improve the performance of the models of Orme et al. [32] and Pitz et al. [29]. Vasu et al. [35] used the same two mechanisms as well as an early version of the model from Politecnico di Milano (PoliMi), which provided best agreement with the high-temperature experiments, however, only Pitz et al. model [29] was able to reproduce the NTC behavior. In addition, PoliMi model was found in the best agreement with a set of OH profiles measured during MCH oxidation behind reflected shock waves [24]. The work of the Stanford group [24,35] was continued in [36], where new shock-tube ignition data were accompanied by OH and H_2O time histories, and performance of the JetSurf 1.1 mechanism was analyzed. The authors concluded that the rate constants for H-abstraction from certain hydrocarbons by OH might have been a reason for the observed differences between experiments and modeling. Tian et al. [37] measured ignition delays of methylcyclohexane in a shock tube at high temperatures, $T = 1075–1724$ K, and simulated their results using four models: JetSurF 2.0 [39], Orme et al. [32], Silke et al. [33] and Wang et al. [22], which all showed similar performance. Note that the model of Silke et al. [33] contains methylcyclohexane sub-mechanism from Pitz et al. [29].

Flames of methylcyclohexane in different configurations were also studied by several research groups. McEnally and Pfefferle [40] investigated methylcyclohexane decomposition in laminar diffusion flames. The groups of Seshadri and Ranzi studied extinction and auto-ignition in counterflow diffusion flames [14,16,41] and tested the Politecnico di Milano detailed reaction mechanism for jet fuel surrogates. Dooley et al. [9] measured extinction strain rate in the counterflow burner and species profiles in a flow reactor for a surrogate fuel containing 22.5% methylcyclohexane to study the influence of cycloalkane functionality. The authors also selected the PoliMi mechanism to simulate their results. Liu et al. [42] used similar experimental configuration to measure ignition temperatures at local strain rate of 120 s^{-1} and found predictions of the JetSurF 2.0 model [39] in satisfactory agreement with the experiments.

Skeen et al. [43] measured stable species and identified several new C_6 and C_7 isomers in low pressure MCH flames using molecular beam mass spectrometry and observed discrepancies with simulations obtained using Pitz et al. mechanism [29]. Wang et al. [22] developed a new kinetic model validated using methylcyclohexane decomposition products in a flow reactor and species concentrations in a low-pressure flame. This model was also tested against experimental data from the literature on ignition delays and laminar burning velocities of MCH.

The laminar burning velocity, S_L, of methylcyclohexane was investigated in spherical and counterflow flame configurations. Kumar and Sung [44] obtained S_L at atmospheric pressure and initial temperature of 400 K using the counterflow technique and linear stretch correction. Ji and co-workers [45,46] also implemented counterflow configuration, yet the stretch-correction was performed using so-called computationally-assisted technique. The authors determined S_L at atmospheric pressure and initial temperatures of 353 K [45] and 403 K [46]. They also performed detailed kinetic modelling and found predictions of the JetSurf 1.1 model in good agreement with their experiments. Wu et al. [47] investigated expanding spherical flames from 1 up to 20 atm and initial temperature of 353 K using non-linear stretch correction. At atmospheric pressure they found reasonable agreement with the data of Ji et al. [45], yet some discrepancies were observed in lean and rich flames. Wu et al. [47] tested JetSurf 2.0 model [39], which moderately overpredicted burning velocities of methylcyclohexane + air flames especially at atmospheric pressure.

As will be shown in the following existing datasets of the MCH burning velocity are not consistent that hampers validation of detailed kinetic models. Therefore the goals of the present collaborative study were: (a) to provide new experimental data on the laminar burning velocity of methylcyclohexane over an extended range of initial temperatures including conditions visited in the previous studies [44–47]; (b) to compare these data with predictions of kinetic models used in literature: JetSurf 2.0 [39] and the current version of the Politecnico di Milano mechanism [48] were selected. Experiments have been performed at Lund University and at Samara National Research University using the same technique, the heat flux method, yet on experimental rigs of different design.

2. Experimental details

The determination of the laminar burning velocity was performed employing the heat flux method. A review of the method and its development, description of the experimental setup at Lund University and of the data processing algorithm were presented in the recent paper [49]. One of the goals of the present collaborative study was to compare the laminar burning velocity measured on two experimental setups in Samara National Research University and Lund University, therefore, the differences between the two setups and modifications from [49] will be outlined.

The heat flux method allows stabilization of flat adiabatic flames on a perforated burner. To achieve adiabaticity, the burner plate must be kept at a temperature higher than the temperature of the plenum chamber of the burner. These two temperatures are controlled using water or oil circuits and two circulator baths. The design of the plenum chamber ensures that the gas mixture reaches the required initial temperature T_g which was set in the range 298–400 K. Specifically, in Samara, temperatures of 298, 318, 338 and 353 K were investigated using circulator baths Grant TXF-200 run on water. In Lund, T_g was set to 298, 353 and 400 K with Grant GD120 water circulators or Julabo MA-4 baths run on oil.