



Laminar flame speeds of cyclohexane and mono-alkylated cyclohexanes at elevated pressures

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ARTICLE INFO

Article history:

Received 26 October 2011

Received in revised form 19 November 2011

Accepted 20 November 2011

Available online 10 December 2011

Keywords:

Laminar flame speeds

Elevated pressures

Cyclo-alkanes

Naphthenes

Mono-alkylated cyclohexanes

Fuel surrogates

ABSTRACT

The propagation speeds of expanding spherical flames of cyclohexane, methylcyclohexane and ethylcyclohexane in mixtures of oxygen/inert were measured in a heated, dual-chamber vessel, with the corresponding laminar flame speeds extracted from them through nonlinear extrapolation. Measurements were conducted at atmospheric and elevated pressures up to 20 atm. Computational simulations were conducted using the JetSurF 2.0 mechanism, yielding satisfactory agreement with the present measurements at all pressures, with a slight over-prediction at 1 atm. Measurements reveal the following trend for the flame speeds: cyclohexane > *n*-hexane > methylcyclohexane \approx ethylcyclohexane at all pressures, with the maximum difference being approximately 5% at 1 atm and 13% at 10 atm. Examination of the computed flame structure shows that owing to its symmetric ring structure, decomposition of cyclohexane produces more chain-branching 1,3-butadiene and less chain-terminating propene. On the contrary, a more balanced distribution of intermediates is present in the flames of methylcyclohexane and ethylcyclohexane due to substitution of the alkyl group for H.

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1. Introduction

Cyclo-alkanes are components of commercial fuels such as jet fuel which typically has around 20% of cyclo-alkanes by volume [1]. Some alternative fuels, particularly those derived from coal [2], are almost entirely composed of cyclo-alkanes. However, the combustion characteristics and oxidation kinetics of cyclo-alkanes have not been studied as extensively as *n*-alkanes.

There have been relatively few measurements of the laminar flame speeds for cyclo-alkanes. Most data were obtained at atmospheric or slightly elevated pressures. Specifically, Davis and Law [3] measured the laminar flame speeds for cyclohexane and cyclopentane at atmospheric pressure and unburned gas temperature of 298 K; Farrell et al. [4] measured those of cyclohexane, cyclopentane, and methylcyclopentane at 3 atm and 450 K; Dubois et al. [5] measured those of *n*-propylcyclohexane at 403 K and atmospheric pressure; and Ji et al. [6] measured those of cyclohexane, methyl-, ethyl-, *n*-propyl- and *n*-butyl-cyclohexanes at 353 K and atmospheric pressure.

Cyclohexane and its mono-alkylated derivatives have been selected as representative cyclo-alkane components of surrogate jet fuels [2], gasoline [7] and diesel [8]. Several kinetic models have been proposed, such as the semi-detailed models for cyclohexane and methylcyclo-

hexane by Ranzi and co-workers [9–11], the kerosene model by Dagaut and co-workers [12] which includes the kinetics of cyclo-alkanes, and Westbrook and co-workers' models for cyclohexane and methylcyclohexane [13,14]. Recently, a detailed high-temperature model, JetSurF 2.0 [15], has been developed which includes the kinetics of cyclohexane and mono-alkylated cyclohexanes. The performance of JetSurF 2.0 in predicting the laminar flame speeds of cyclohexane and mono-alkylated cyclohexanes has been well validated at atmospheric pressure in [6]; however, its performance at elevated pressures has not been evaluated.

The fundamental understanding on the decomposition and further oxidation of cyclo-alkanes is also of interest. Studies of the laminar flame speeds of C₅–C₈ alkanes [3,16,17] showed that they are almost identical. The reason for this fuel similarity has been attributed [17] to the fact that *n*-alkanes all crack into similar small fragments (C₀–C₄) in flames due to their similar straight-chain molecular structure. However, this fuel similarity does not seem to exist for cyclo-alkanes from the measurements of Ji et al. [6], in which the following trend was found for the flame speeds: cyclohexane > *n*-hexane > mono-alkylated cyclohexanes. Using numerical simulation, Ji et al. [6] attributed the difference between *n*-hexane and cyclohexane to thermal effects, *i.e.*, the small difference in the adiabatic flame temperatures, and the difference between cyclohexane and its mono-alkylated derivatives to chemical kinetic effects caused by the change in the distribution of smaller molecules formed when the original fuel molecules decompose. In particular, mono-alkylated cyclohexane was found to form more propene while

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cyclohexane more 1,3-butadiene. The former would lead to chain terminating reactions while 1,3-butadiene would lead to chain branching, resulting in a lower flame speed for the mono-alkylated cyclohexanes as opposed to cyclohexane.

The present study aims to provide archival laminar flame speed data for cyclohexane, methylcyclohexane and ethylcyclohexane at pressures from 1 atm to 20 atm at the initial temperature of 353 K. These measurements will allow us to investigate the pressure effect on the flame propagation of cyclohexane and its mono-alkylated derivatives; for instance whether the effect of alkyl group substitution on the laminar flame speed still holds at elevated pressures. Furthermore, substantial data at various conditions also allow for further understanding of the thermal decomposition and oxidation of cyclo-alkanes.

2. Experimental specifications

2.1. Experimental setup

Laminar flame speeds were determined using expanding spherical flames. Since detailed descriptions and dimensions of the experimental apparatus, procedure and data analysis were reported in two previous publications [17,18], only a brief description of the experimental apparatus and procedure is provided here.

The apparatus consists of a cylindrical chamber radially situated within another cylindrical chamber of substantially larger volume. The wall of the inner chamber is fitted with a series of holes that can be mechanically opened and closed to allow the union and separation of the gases in the inner and outer chambers. The outer chamber is covered with silicon electrical heaters, hence enabling it to act as an oven to uniformly heat the inner chamber to a given temperature, which is 353 K and is the initial gas temperature for all of the present data.

The experimental procedure involves first filling the inner chamber with fuel vapor produced by heating a liquid fuel reservoir maintained at 353 K, followed by a certified mixture of oxidizer and inert gas which is also preheated to at least 353 K. The desired equivalence ratio in the inner chamber is obtained by monitoring the partial pressures of the gases in the inner chamber. The outer chamber is filled with a mixture of inert gases to match the pressure and density of the gas in the inner chamber.

After filling the inner and outer chambers, the inner chamber gases are thoroughly mixed using a series of fans and pumps to ensure homogeneity. The gas is then allowed to settle briefly before it is spark ignited. Concurrent to this instant, the holes between the inner and outer chambers are opened, resulting in an expanding spherical flame that propagates throughout the inner chamber in essentially an isobaric environment before it is quenched upon contacting the inert gases of the outer chamber. The flame surface is visualized using a pin-hole Schlieren system coupled to a high-speed camera running typically at 10,000 frames per second.

As a secondary check of the gas composition in the inner chamber, samples of the gas in the tubing connected to the inner chamber are analyzed using a gas chromatograph with a flame ionization detector. All gas samples were verified to have less than a 2% random error in the equivalence ratio, as is expected based on the gas filling procedure.

2.2. Data analysis

Tracking the flamefront yields the history of the radius of the spherical flame as a function of time, $r_f(t)$. For extrapolation of the laminar flame speed from $r_f(t)$, the relation recently derived by Kelley et al. [19] is employed,

$$S_b^0 t + C = r_f + 2L_b \ln r_f - \frac{4L_b^2}{r_f} - \frac{8L_b^3}{3r_f^2} \quad (1)$$

where S_b^0 is the adiabatic, unstretched gas speed of the burned mixture relative to the flame, r_f the flame radius, L_b the Markstein length, t the time and C a constant accounting for the initial conditions. With S_b^0 the laminar flame speed, S_u^0 can then be calculated from the continuity relation,

$$\rho_u^0 S_u^0 = \rho_b^0 S_b^0 \quad (2)$$

where ρ_u^0 and ρ_b^0 are respectively the densities of the unburned and burned mixtures. It is noted that Eq. (1) contains up to the third-order accuracy in terms of the inverse flame radius. Other extrapolation relations, such as the linear model [20], nonlinear model with quasi-steady approximation [21] and the Markstein's empirical equation [22] only contain up to first or second order accuracy. While the flame speeds extrapolated from the linear model [20] are generally higher than that from the quasi-steady nonlinear model [21], for both $Le > 1$ and $Le < 1$ cases, using Eq. (1) leads to results between the two, and is much closer to those of the latter [21]. For typical hydrocarbon fuels, using Eq. (1) and the quasi-steady nonlinear relation [21] leads to a maximum difference of only approximately 1 cm/s, with the difference increasing as the equivalence ratio deviates from the value corresponding to zero Markstein number.

We further note that for flame speed measurements using expanding spherical flames, the data selected for extrapolation need to be in a certain radius range in that the small and large radius data are respectively contaminated by the influences of ignition and the chamber confinement, as discussed in details in [23–26]. For our experimental setup and the choice of fuels studied, a conservative assessment of this range is between radii of 1.0 and 1.8 cm. The actual selected data for extrapolation at each data point was within this range, assisted by assessment of the trajectories of dr_f/dt versus stretch rate, $(2/r_f)dr_f/dt$. Based on repeated measurements and the sensitivity of slight variation of the data selection, all reported laminar flame speeds in this paper have an uncertainty of approximate ± 2 cm/s.

2.3. Numerical approach

For quantitative comparison and mechanism studies, numerical computation was performed using the Chemkin Premix code [27] to determine the computed laminar flame speeds as well as detailed flame structure. All calculations used multi-component formulation for transport properties including Soret diffusion. The calculation used finite difference method with adaptive gridding, which was refined until a grid-independent solution was found.

The present study uses the JetSurF 2.0 mechanism developed by Wang et al. [15], which includes 348 species and 2163 reactions. There are also other existing mechanisms [9–14]; however, since the focus of the paper is on providing experimental data, JetSurF 2.0 was selected as an example for comparison. Indeed, it is also the only mechanism that can simulate the combustion of ethylcyclohexane so far.

3. Results

3.1. Validation of present approach

In order to assess the validity of the present approach, we shall first compare the laminar flame speeds with those in the literature. For *n*-heptane at atmospheric pressure, which has been extensively studied in the literature, four independent measurements can be used for comparison: the data of Kelley et al. [17] obtained using

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