Journal of Hazardous Materials 321 (2017) 440–448

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Inert gas influence on the laminar burning velocity of methane-air mixtures

Maria Mitu[a], Venera Giurcan[a], Domnina Razus[a,*], Dumitru Oancea[b]

[a] "Ilie Murgulescu" Institute of Physical Chemistry, 202 Spl. Independentei, Bucharest, Romania
[b] University of Bucharest, Department of Physical Chemistry, 4-12 Blvd. Elisabeta, Bucharest, Romania

HIGHLIGHTS

- Laminar burning velocities of CH_4-air-inert (He, Ar, N_2, CO_2) mixtures are reported.
- The experimental burning velocities are examined in comparison to computed ones.
- The influence of pressure and equivalence ratio on burning velocities is examined.
- The overall reaction order and overall activation energy of CH_4-O_2 reaction are reported.

ARTICLE INFO

Article history:
Received 17 June 2016
Received in revised form 25 August 2016
Accepted 14 September 2016
Available online 14 September 2016

Dedicated to the 150th anniversary of the Romanian Academy.

Keywords:
Laminar burning velocity
Methane
Inert additive
Overall activation parameters

ABSTRACT

Flame propagation was studied in methane-air-inert (He, Ar, N_2 or CO_2) mixtures with various initial pressures and compositions using pressure-time records obtained in a spherical vessel with central ignition. The laminar burning velocities of CH_4-air and CH_4-air-inert mixtures obtained from experimental $p(t)$ records of the early stage of combustion were compared with literature data and with those obtained from numerical modeling of 1D flames. The overall reaction orders of methane oxidation were determined from the baric coefficients of the laminar burning velocities determined from power-law equations. For all mixtures, the adiabatic flames temperatures were computed, assuming that the chemical equilibrium is reached in the flame front. The overall activation energy for the propagation stage of the combustion process was determined from the temperature dependence of the laminar burning velocity.

1. Introduction

The depletion of crude oil reserves and persistent requirements for cleaner combustion of fossil fuels have driven the wide use of natural gas as an alternative fuel for use in internal combustion engines (ICE) and power generation. Because the main constituent of natural gas is methane, investigation of its combustion characteristics is of great importance. Numerous studies on methane flames have focused on understanding the fundamentals of combustion in terms of ignition and extinction, propagation speed and burning velocity, dynamic behavior or instabilities, and kinetic mechanisms, among others. An important component of such studies is the determination of laminar burning velocity, which is a fundamental parameter of combustion that depends on the rate of reactions occurring in the flame and the thermo-physical properties of the flammable mixture. Numerous studies have focused on methane combustion in flames, resulting in a large body of measured and computed burning velocities at ambient initial conditions or under ICE operating conditions. Many of these data were obtained from closed vessel experiments, using synchronous records of the pressure and flame radius and applying suitable corrections for flame stretch and curvature in the early stage of combustion and for heat losses from the flame front in the late stage of combustion. A great advantage of this method is the possibility of obtaining burning velocities at pressures and temperatures different from ambient conditions. Besides this, one can evaluate the influence of pressure and temperature on the laminar burning velocity from the data of a single experiment, since the transient

* Corresponding author.
E-mail addresses: drazus@icf.ro, drazus@yahoo.com (D. Razus).

http://dx.doi.org/10.1016/j.jhazmat.2016.09.033
0304-3894/

burning velocities refer to variable temperature and pressure of the unburnt gaseous mixture [1–6]. Improved values of laminar burning velocities for CH_4-air mixtures corrected for flame stretch were reported in recent studies using outwardly propagating spherical laminar flames monitored by optical methods only a short time after ignition, when the disturbances caused by the energy input at ignition, the flame curvature, and the varying flame thicknesses are small [2,7–21]. Other models used only $p(t)$ measurements over longer periods, i.e., from ignition up to the inflection point $p(t)$ records. The laminar burning velocities of CH_4-air mixtures were determined using models for either thin flames [3,4,22,23] or thick flames [3,5,24,25]. Stationary flames anchored on burners were also used to determine the laminar burning velocity of methane with air or air + inert additives using the heat flux method [26–31]. Stagnation flames allowed determination of stretch-free laminar flame speeds of CH_4-air mixtures over extensive ranges of stoichiometry, pressure, and flame temperature [32–34]. Another recent method used data obtained in a preheated high-aspect-ratio diverging channel [35]. All recent studies delivered a reference value of $(37 \pm 1)\,cm\,s^{-1}$ for the stretch-corrected laminar burning velocity of the stoichiometric CH_4-air mixture at ambient initial conditions. For measurements at pressures and/or temperatures different from ambient conditions, a higher spread of laminar burning velocities exists despite the advanced corrections.

The wide use of natural gas as an alternative fuel has promoted numerous studies on flame propagation in methane-air mixtures diluted by inert gases because natural gas contains inert components such as N_2 or CO_2 [8,13,15,19,22–24,27,30–32,36–41]. At the same time, the use of inert gases as suppressants for methane-air explosions explains the growing number of experimental and computational studies on flame propagation and quenching. The combustion of methane in the presence of inert gases (including water (vapor)) was studied in connection to the EGR (exhaust gas recirculation) technique, which was intended to lower combustion instabilities and reduce NOx emissions and the rate of heat transfer in engines [15,39]. At the same time, the need for adequate and reliable safety recommendations have driven research on flame propagation in methane-air mixtures diluted by inert gases. Taken together, these reasons explain the growing interest in reliable values of laminar burning velocities for CH_4-air and CH_4-air-inert mixtures under various initial conditions. Recent review articles have presented the state of this problem and outlined the need to examine and improve the predictions from various chemical modeling packages by comparing the experimental and computed burning velocities [42,43].

The aim of this paper is to complete these studies with measurements of the laminar burning velocities of methane-air and methane-air diluted with He, Ar, N_2 and CO_2 determined from pressure measurements in a spherical vessel with central ignition in the early stage of flame propagation. For CH_4-air, experiments were conducted on mixtures with various initial pressures and compositions at ambient temperature. For CH_4-air-inert mixtures, experiments were performed at ambient pressure and temperature using CH_4-air with various methane-air ratios and variable inert gas contents. The laminar burning velocities obtained from experiments are compared with the burning velocities from detailed numerical modeling of 1D methane-air and methane-air-inert flames based on the GRI mechanism (version 3.0) and propagated under the same initial pressures and compositions. Using the correlations of laminar burning velocity with pressure and average flame temperature, the overall reaction orders of methane oxidation and the overall activation energy for the propagation stage of the combustion process were determined. They represent valuable input data for CFD (Computational Fluid Dynamics) modeling of flame propagation in various enclosures.

2. Experimental

Experiments were conducted in a spherical closed vessel ($V = 0.52$ L) with central ignition via inductive-capacitive sparks produced between stainless steel electrodes. A spark gap of constant width (3.5 mm) was located in the geometrical center of the spherical vessel.

The explosion was monitored using pressure measurements collected with a piezoelectric transducer Kistler 601A connected to a Charge Amplifier Kistler 5001SN coupled with an acquisition data system TestLab™ Tektronix 2505. The flame front position was determined using an ionization probe immersed at various depths in the vessel. The data acquisition was conducted at 7000 signals/s.

A vacuum and gas-feed line (which was gastight at pressures between 0.5 mbar and 5 bar) connected the explosion vessel with the gas cylinders containing fuel, air and the inert gas, the metallic cylinder for mixture storage and a vacuum pump. Before each test, the combustion vessel was evacuated to 0.5 mbar, and the explosive mixture was admitted and allowed to reach quiescence. Other details were previously reported [44–46].

CH_4-air mixtures were prepared in a 10 L storage cylinder using the partial pressure method at a total pressure of 4 bar. CH_4-air-inert mixtures were prepared directly in the combustion vessel by addition of the inert gas to any CH_4-air mixture at the appropriate partial pressures to reach the total initial pressure of 1 bar. Before ignition, the flammable mixtures were allowed to mix and become quiescent for 30 min. The average standard error observed in partial pressure measurement was 1% for CH_4 and 0.5% for inert gases.

Methane (99.99%), He (99.9999%), Ar (99.9999%), N_2 (99.99%), and CO_2 (99.99%) (SIAD Italy) were used without further purification.

Measurements using CH_4-air mixtures were collected at initial pressures between 0.5 and 2.0 bar. Measurements using CH_4-air-inert mixtures were collected at ambient initial pressure using inert concentrations within 0–40% (He, Ar, N_2) and 0–30% (CO_2) (all concentrations are given in vol/vol%).

For each experimental condition, the test was repeated 3–5 times to verify data accuracy and repeatability. The average standard error observed in explosion pressures was 2%, in the cubic law coefficients was 2.5% and was less than 3.5% in the corresponding burning velocities.

3. Computing program

The adiabatic flame temperatures and adiabatic explosion pressure of flammable mixtures were calculated using the COSILAB 0-D program [47] with the assumption that the thermodynamic equilibrium is reached within the flame. This program is based on a general algorithm for computing the equilibrium composition of products for fuel-oxidizer gaseous mixtures by determining the minimum of the free enthalpy (isobaric combustion) or free energy (isochoric combustion).

Kinetic modeling of one-dimensional, premixed laminar free flames was performed with the COSILAB 1-D package (version 3.0.3) which uses preprocessors that accept molecular and thermodynamic data and reaction mechanisms compatible to the international standard format put forward by Sandia National laboratories. As solvers, the package uses a steady Newton solver (usually 25 iterations, relative tolerance 10^{-5}; absolute tolerance 10^{-8}), an unsteady Newton solver (usually 15 iterations, relative tolerance 10^{-4}; absolute tolerance 10^{-6}) and an unsteady Euler solver. For the adaptive grid parameters, we used GRAD = 0.1, CURV = 0.2 and maximum ratio of adjacent cell size between 1.3 and 1.1. The modeling used GRI (Gas Research Institute) mechanism version 3.0 [47]. This mechanism, in which 53 chemical species and