Propagation Velocities of Propane-air Deflagrations at Normal and Elevated Pressures and Temperatures

VENERA BRINZEA1, MARIA MITU1, CODINA MOVILEANU1, ADINA MUSUC1, DOMNINA RAZUS1,*, DUMITRU OANCEA2

1 “Ilie Murgulescu” Institute of Physical Chemistry, 202 Spl. Independentei, 060021, Bucharest, Romania
2 University of Bucharest, Department of Physical Chemistry, 4-12 Regina Elisabeta Blvd., 030018, Bucharest, Romania

The study of spherically expanding flames in closed vessels affords the calculation of propagation velocity $S_s$ for deflagrations of flammable gaseous mixtures, defined as the flame front velocity in respect to a fixed coordinate system (the explosion vessel). The calculation is based on normal burning velocities $S_n$ obtained from records of pressure variation during the early stage of flame propagation. In the present contribution, propane-air mixtures of variable composition ($\text{[C}_3\text{H}_8\text{]} = 2.5 - 6.2 \text{ vol.\%}$) were studied, at various initial pressures within 0.3 and 1.3 bar and various initial temperatures (within 298 and 550 K). The propagation velocities of examined systems, extrapolated to initial conditions (incipient stage of flame development) obtained from experimental data are examined against propagation velocities obtained from kinetic modelling of propane-air propagation by means of two packages (INSFLA, which used the mechanism developed by Warratz for combustion of C1-C4 hydrocarbons and COSILAB, using GRI mechanism developed by the Gas Research Institute for combustion of C1-C3 alkanes).

Keywords: deflagration; propagation velocity; burning velocity; propane

The propagation velocity of a flame, in either confined or unconfined conditions, is a most important parameter for assessing risk conditions in operating chemical reactors where flammable mixtures are formed, for design of active safety devices (vents) and explosion proof vessels and for mitigation of explosion damaging effects.

The propagation velocity of a flame (space velocity; flame speed) $S_s$ is defined as the velocity of the flame front in respect to the vessel where combustion takes place, i.e. a fixed reference system [1,2]. The propagation velocity is related to $S_n$, the normal burning velocity, another important parameter of flame propagation [1,2]:

$$S_s = S_n + S_g \quad (1)$$

where $S_g$, the gas velocity, is the velocity of the flame front determined by the expansion of the burnt gas behind the flame front and the compression of the unburnt gas ahead of it. The normal burning velocity $S_n$ is the component normal on the flame front surface of the displacement velocity of the flame front in respect to the unburnt gas.

Most studies on flame propagation were focused on measuring or computing the normal burning velocity $S_n$, which is relevant for the overall reaction rate between fuel and oxidizer and may be used for validation of reaction mechanisms or for computing the heat release rate in various conditions. All experimental or computing methods for $S_n$ determination deliver also the propagation velocity, $S_s$. The two characteristic propagation velocities are related by equation [2,3]:

$$S_s = E_o \cdot S_n \quad (2)$$

where $E_o$ is the expansion coefficient of the unburnt gas of constant-pressure combustion, defined as the ratio of the unburnt and burnt gas densities:

$$E_o = \frac{\rho_u}{\rho_b} = \left(\frac{T_{f,p}}{T_0}\right) \left(\frac{n_f}{n_o}\right) \quad (3)$$

with $T_{f,p}$ - the adiabatic flame temperature of isobaric combustion, $n_o$ - the initial mole number and $n_f$ - the final (end) mole number, readily available by equilibrium computations on flames.

The atmospheric fuel-air flames are well characterized both by $S_n$ and/or $S_s$ from experimental methods using steady or unsteady flames. Less information is available on flame propagation at non-atmospheric conditions, especially at high pressures and temperatures.

In the present paper, we examine propane-air flames propagating at various initial pressures between 0.3 and 2.0 bar and various initial temperatures between 298 and 550 K. Propagation velocities $S_s$ of propane-air flames are determined from burning velocities $S_n$ obtained either from experiments in a closed spherical vessel or from kinetic modeling of premixed laminar flames. Propane was chosen as a test fuel, since it is commonly used in IC engines, oxy-gas torches and residential central heating. Propane-air explosions have been widely studied by many authors, who reported explosion pressures [4-7], maximum rates of pressure rise during confined explosions [8-11] and normal burning velocities [12-15]. The propagation velocities of propane-air in various initial conditions complete thus our previous works on flammability characteristics of propane-air gaseous mixtures [6,11,15-17].

Experimental part

A vacuum and gas-feed line forms the experimental set-up, tight at pressures from 0.1 mbar to 2.5 bar. The line interconnects the vacuum pump, the gas cylinders with fuel and air, the metallic cylinder for mixture storage and the explosion vessels. The vacuum pump maintains a vacuum of 0.1 mbar in the explosion vessel, after each experiment.

The fuel–air mixtures were obtained by the partial pressure method and used 48 h after mixing, at a total pressure of 4 bar.

---

* email: drazus@icf.ro; Tel: +40-21-31679 12
Experiments were performed in a thermostated spherical explosion vessel, electrically heated, with central ignition, equipped with an ionization probe. Its temperature was adjusted (± 1°C) using an AEM 1RT36 controller and monitored by a K-type thermocouple. Other details referring to this vessel were previously given [6,11].

The initial pressures of fuel–air mixtures were measured by a strain gauge manometer (Edwards type EPS-10HM). Ignition was made with inductive—capacitive sparks produced between stainless steel electrodes and the spark gap of constant of 3.5 mm was located in the geometrical center of vessel. The pressure variation during explosions was recorded with a piezoelectric pressure transducer (Kistler 601A) mounted in a special adapter, maintained at (25 ± 0.5)°C by a water jacket. The pressure transducer was connected to a Charge Amplifier (Kistler 5001SN). The signals of the ionization probe amplifier and of the Charge Amplifier were recorded with an acquisition data system TestLabTM Tektronix 2505, by means of an acquisition card type AA1, usually at 5000 signals/s.

Propane (99.99%) (SIAD Italy) was used without a further purification.

Computer programs

ECHIMAD [18] program was used for calculation of adiabatic flame temperatures in isobaric combustion, assuming that the thermodynamic equilibrium is reached within the flame. The calculations were made for various initial temperatures within 300-550 K. The 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. Fifteen compounds (C graphite, O 2, N 2, H 2O, CO, CO 2, H 2, NO, CH 4, C2H2, C3H8, C4H10, H, OH and O) were taken into account. The heat capacities (expressed as \( C_p = f(T) \) polynomials), the standard enthalpies of formation at 298 K and the standard entropies at 298 K were taken from literature [19].

The kinetic modelling of propane-air laminar adiabatic premixed flames in various conditions was made by means of INSFLA and COSILAB packages. In both cases, the runs were performed for the isobaric combustion at 1 bar initial pressure and various initial temperatures within 300-550 K. INSFLA was run using the mechanism developed by Warnatz for combustion of \( C_nH_m \) hydrocarbons (53 chemical species, 592 elementary reactions) [20-22]. Updated values of several rate coefficients, for the rate-limiting reactions in propane-air oxidation were taken from Heghes [23]. COSILAB was run using the GRI 3.0 mechanism (53 chemical species and 325 elementary reactions) [24]. The runs were performed for isobaric combustion of propane-air mixtures at various initial pressures within 0.5 and 3 bar and various initial temperatures within 300 – 550 K. The input data were taken from thermodynamic and molecular databases of Sandia National Laboratories, USA, according to the international standard (format for CHEMKIN).

Results and discussions

The propagation velocities \( S_p \) of propane-air flames were determined from the normal burning velocities \( S_n \) and the expansion factors \( E_0 \) according to equation (2).

In figure 1 relevant values of the adiabatic flame temperatures \( (T_f,p) \) for \( C_nH_m \)-air mixtures burning at constant pressure and various initial temperatures are given. The corresponding expansion coefficients of propane-air mixtures at ambient initial pressure and various initial temperatures are given in figure 2.

The experimental values of normal burning velocities \( S_n \) characteristic to the initial moment of propane-air explosions were obtained from pressure records obtained in the early stage of flame propagation \( (\Delta p \leq p_f) \) in a spherical vessel with central ignition, using the cubic law of pressure rise versus time, as reported in earlier papers [15,16]. A set of representative values of normal burning velocities \( S_n \) and propagation velocities \( S_p \) obtained from experimental \( p(t) \) records in a stoichiometric propane-air mixture, at variable initial pressures, is given in table 1. Both normal burning velocity and propagation velocity decrease when initial pressure increases. The dependence of propagation velocities \( S_p \) on pressure \( p \) was written as a power law:

\[
S_p = S_{p,ref} \left( \frac{p}{p_{ref}} \right)^\beta
\]

where \( S_{p,ref} \) is the reference value of the propagation velocity, at \( p = p_{ref} \) usually taken as 1 bar. The baric exponent \( \beta \) was calculated by a non-linear regression analysis of data. The baric exponents of propagation velocities for propane-air with a variable propane concentration are close to the baric exponents \( \nu \) of normal burning velocities previously reported [15], a fact determined by the weak dependence of expansion coefficients \( E_0 \) on initial pressure. The same variation of propagation velocities as a result of pressure variation was found for the whole examined mixtures within the flammability range of propane in air. Propagation velocities of methane-air mixtures at variable initial pressures within 0.7 and 4.0 bar reported by Agrawal for \( CH_4\)-air mixtures [25] from photographic records of flame
The propagation velocities of propane-air mixtures at ambient initial conditions determined from experimental data and from kinetic modelling of propane-air flames are plotted against propane concentration in figure 4. A fair agreement is found between experimental propagation velocities and those delivered by kinetic modelling based on GRI mechanism, for all examined systems. The propagation velocities obtained by means of INSFLA package and the modified Warnatz mechanism are close to the other data sets only in the range of rich propane-air mixtures.

The influence of initial temperature on propagation velocities is seen in figure 5, where experimental data were plotted. For all concentrations, the temperature increase determines the increase of propagation velocity. At constant initial pressure and composition, the dependence of propagation velocities on temperature was written in the form of a power law:

$$S_T = S_{\text{ref}} \left( \frac{T}{T_{\text{ref}}} \right)^\alpha$$

where $S_{\text{ref}}$ is the reference value of the propagation velocity at $T=T_{\text{ref}}$, usually taken as 298 K and $\alpha$ is the thermal exponent, calculated by a non-linear regression analysis of data. The thermal coefficients $\alpha$ determined from experimental data range within 1.28 and 1.45; slightly lower values were determined from computed propagation velocities, both from INSFLA and COSILAB runs. For these data sets, the standard errors varied between 3 and 4%, much lower in comparison with standard errors of
experimental thermal exponents, ranging between 5 and 13%. The thermal coefficients $\alpha$ of propagation velocities are lower than the thermal coefficients of normal burning velocities $\mu$, which range usually between 1.6 and 2.0 [15]; this results as a consequence of simultaneous temperature influence on $S$ and $T_0$ which determine the propagation velocity of each flammable mixture according to eq. (2).

Conclusions

The propagation velocities of propane-air flames, strongly dependent on initial concentration, pressure and temperature of flammable mixtures, range between 0.50 - 4.5 m/s.

At constant composition, the pressure and temperature dependence of propagation velocity was written as a power law:

$$S = S_{ref} \left( \frac{T}{T_{ref}} \right)^{\alpha} \left( \frac{P}{P_{ref}} \right)^{\beta}$$

with $\alpha$ (the thermal coefficient) = 1.20 ... 1.50 and $\beta$ (the baric coefficient) = -0.150.... -0.120.

The kinetic modelling predicts normal burning velocities and propagation velocities for a wide range of initial parameters variation. A fair agreement was found between experimental and computed propagation velocities.

The data have a great practical interest for understanding the flame propagation in closed vessels, especially in connection to TDD (transition of deflagration to detonation); and with flashback processes. Such information is necessary for safety recommendations, for running reactors or plants where flammable mixtures are formed.

Acknowledgements: This work was supported by CNCSIS –UEFISCSU, project number PNII – IDEI code 458/2008. The authors gratefully thank Prof. U. Maas (Institut fur Technische Verbrennung, Karlsruhe, Germany) and Dr. D. Markus (PTB, Braunschweig, Germany) for the permission to run the program INSFLA and for the provided assistance.

References

3. BRADLEY, D., MITCHESON, A., Combust. Flame, 26, 1976, p. 201

Manuscript received: 7.10.2011

Table 2

<table>
<thead>
<tr>
<th>$\text{(C}_3\text{H}_8)$ / (vol.%)</th>
<th>$\alpha$ (experimental data)</th>
<th>$\alpha$ (computed data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.61</td>
<td>$1.450 \pm 0.196$</td>
<td>$1.251 \pm 0.049$</td>
</tr>
<tr>
<td>4.02</td>
<td>$1.276 \pm 0.073$</td>
<td>$1.354 \pm 0.055$</td>
</tr>
<tr>
<td>5.06</td>
<td>$1.433 \pm 0.076$</td>
<td>$1.288 \pm 0.047$</td>
</tr>
</tbody>
</table>

http://www.revistadechimie.ro