# TEMPERATURE, PRESSURE AND DILUTION EFFECT
ON LAMINAR BURNING VELOCITY OF PROPANE-AIR

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The flame propagation during the deflagration of stoichiometric propane/air mixtures diluted with 10% inert (N_2, Ar, CO_2) at various initial pressures and temperatures (p_0 = 30–200 kPa, T_0 = 298–423 K) in a spherical vessel with central ignition was monitored by means of pressure measurements. Using an improved relationship for the burnt mass fraction, recently revalidated, the laminar burning velocities were calculated from pressure-time records over an extended duration of spherical propagation. The experimental burning velocities are examined in comparison with computed burning velocities, obtained from a numerical modeling of 1D laminar flames using GRI version 3.0 mechanism. For all data, the diluent influence on burning velocities is discussed.
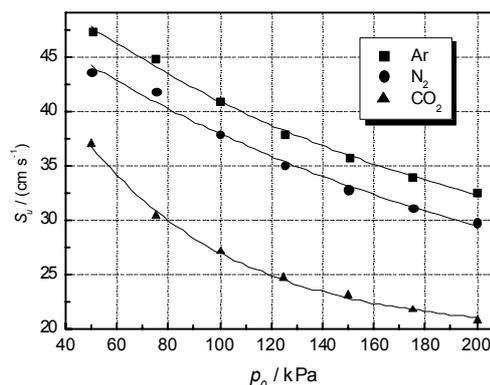
INTRODUCTION

The study of unsteady flame propagation in a spherical vessel with central ignition is widely used for laminar burning velocity determination as it offers a major advantage in comparison with other methods concerning the availability of extended ranges for measurements at various pressures and temperatures. Therefore, flames propagating in non-atmospheric conditions (especially at high pressures and temperatures, where normal burners cannot be used) can be easier studied. Another important advantage stems from the possibility to determine the burning velocity from data of a single experiment, after making 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.

In many studies the synchronous recording of pressure and flame radius offers complementary data on flame propagation through the transient values of the flame radius r_b, space velocity S_s, and normal burning velocity S_u.[1-3] At the same time, procedures based just on transient pressure−time records afford the calculation of normal burning velocity using various models for the burnt mass fraction[4-7] in conjunction with simplifying assumptions meant to obtain an analytical solution for the

normal burning velocity. Recent contributions[8-14] use numerical methods for solving the differential equations obtained using more accurate formulations of the burnt mass fraction. Even in such approaches, simplifying assumptions were made, e.g., neglecting the heat losses toward the end of the process,[11,12] the flame front thickness[13] or the stretch effect, even in the initial stage of the process.[14] Our previous contributions[7,15] described a procedure for burning velocity calculation from transient pressure records in a closed spherical vessel by means of a simple model for the burnt mass fraction valid over an extended duration of flame propagation. Burning velocities of propane-air mixtures at various initial concentrations, pressures and temperatures[15] were found in good agreement with data obtained by other experimental techniques and with results of chemical modeling.

Investigation of propane combustion in air by the spherical bomb technique is completed now by data referring to stoichiometric propane-air-inert mixtures, where Ar, N_2 or CO_2 are the inert components. The paper examines the burning velocities of stoichiometric propane-air mixtures diluted with 10% inert, at various total initial pressures within 30 and 200 kPa and initial temperatures within 298 and 423 K. The burning velocities are discussed in correlation with pressure and temperature, using either data obtained in a single experiment or data obtained in several experiments (when burning velocities extrapolated to initial conditions are acquired). The burning velocities obtained from experiments are compared to burning velocities from a detailed numerical modeling of 1D propane−air laminar flames based on the GRI mechanism, version 3.0, and propagating under the same initial concentrations, pressures, and temperatures.

EXPERIMENTAL

Experiments were made in a spherical explosion vessel with radius R_c = 5 cm, tight up to a static pressure of 4 MPa. The combustion vessel was electrically heated; its temperature was adjusted by ± 1°C using a AEM 1RT96 controller and monitored by a K-type thermocouple. The pressure variation during explosions was recorded with a piezoelectric pressure transducer (Kistler 601A), connected to a Charge Amplifier (Kistler 5001SN) and an Acquisition Data System (Tektronix TestLab 2505) at 10,000 signals/s. The piezoelectric pressure transducer was mounted in a special adapter, maintained at (25 ± 0.1)°C by a water jacket. A vacuum and gas feed line, tight at pressures between 50 Pa and 500 kPa, connected the combustion vessel with the gas cylinders containing fuel, air

and the inert gas, the metallic cylinder for mixture storage and a vacuum pump. The fuel–air–inert gaseous mixtures were obtained in metallic cylinders, at a total pressure of 500 kPa, by the partial pressure method and used 24 h after mixing the components. Details on the experimental set-up and procedure were previously given.[16-18]

Propane (99.99%), Ar (99.99%), N_2 (99.99%) and CO_2 (99.5%) were purchased from SIAD, Italy and used without further purification.

DATA EVALUATION

The flame radius $r_b = R_c \cdot [1 - (1-n) \cdot \pi^{-1/\gamma_u}]^{1/3}$ and the normal burning velocity $S_u = \dfrac{R_c^3}{3 r_b^2} \left(\dfrac{1}{\pi}\right)^{1/\gamma_u} \dfrac{dn}{dt}$ were calculated from the transient pressure records in the spherical vessel using the basic equations developed by Manton, Lewis & von Elbe.[19] Here, r_b is the instantaneous flame radius (at pressure p), R_c is the radius of the explosion vessel, n is the burnt mass fraction, γ_u is the adiabatic compression coefficient of the unburnt gas; π is the relative pressure, defined as $\pi = p/p_0$ with p - the transient pressure (at time t) and p_0 - the initial pressure. The burned mass fraction was calculated according to O'Donovan[4] as $n = \dfrac{\theta \cdot (\pi - \pi^{1 - 1/\gamma_u})}{\pi_e - \theta \cdot \pi^{1 - 1/\gamma_u}}$,

where $\theta = \dfrac{\overline{T_{f,e}}}{\overline{T_{f,p}}}$, with $\overline{T_{f,p}}$ - the average burned gas temperature at time t and pressure p and $\overline{T_{f,e}}$ - the average end burned gas temperature. According to our previous studies[7,15] the transient relative burnt gas temperature θ was expressed as a function of transient pressure π by a power law, similar in form to the adiabatic compression law: $\theta = \left(\pi_e / \pi\right)^{1 - 1/\gamma^*}$. The initial relative temperature of the burned gas is $\theta_0 = T_{f,V}/T_{f,p}$ and the end relative temperature of the burned gas is $_e$ 1, where $T_{f,p}$ is the adiabatic flame temperature of isobaric combustion at $p = p_0$ and $T_{f,V}$ is the adiabatic flame temperature of isochoric combustion at p p_0. The parameter γ^* is a composite parameter, calculated as: $\gamma^* = \ln \pi_e / \ln\left(\pi_e / \theta_0\right)$. The data from the early stage of explosion propagation (within the interval

p_0....1.5 p_0) have been left aside, in order to avoid the disturbing effects of flame stretch and curvature on normal burning velocity during this stage. Data evaluation was carried out up to the inflection point of $p(t)$ records, when usually the heat losses towards the vessel become significant.

The adiabatic flame temperatures of isobaric and isochoric combustion for propane-air mixtures at various initial temperatures within 300–550 K and various initial pressures within 50–300 kPa were calculated with the 0-D COSILAB package. The program is based on a general algorithm meant to compute the equilibrium composition of products for any fuel–oxidizer gaseous mixture using the thermodynamic criterion of chemical equilibrium: the minimum of Gibbs energy, at constant temperature and pressure or minimum of Helmholtz energy, at constant temperature and volume. Fifty-three compounds were considered as combustion products.

CHEMICAL KINETIC MODELING

The laminar burning velocities of gaseous mixtures were computed by means of 1-D COSILAB package, developed by Rogg and Peters for kinetic modeling of fuel-air flames in various conditions.[20] In the present case, premixed laminar free flames were examined, assuming radiative energy losses. The runs used GRI 3.0 mechanism, based on 53 chemical species which participate to 325 elementary reactions. 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 DISCUSSION

Measured burning velocities

Typical plots of burning velocity variation against pressure during several single experiments are given in Fig. 1. In each experiment, the burning velocity S_u has a monotonous variation against pressure or unburnt gas temperature, T_u.

The pressure influence on S_u was modeled by a simple power law: $S_u = S_{u,0}\,\pi^{\varepsilon}$, where $S_{u,0}$ is the burning velocity at the initial moment (p_0 and T_0), π is the dimensionless pressure and ε is a composite parameter named the "thermokinetic coefficient". The thermokinetic coefficient is closely bound to the baric and the thermal exponents of the burning velocity   and   , respectively) used to model the initial pressure and temperature influence on burning velocities by power law:[2]

$$\varepsilon = \nu + \mu\left(1 - \frac{1}{\gamma_u}\right) \qquad (1)$$

$$S_u = S_{u,ref}\left(\frac{T}{T_{ref}}\right)^{\mu}\left(\frac{p}{p_{ref}}\right)^{\nu} \qquad (2)$$

when the law of adiabatic compression: $T_u = T_{ref}\left(\dfrac{p}{p_{ref}}\right)^{1-\frac{1}{\gamma_u}}$ is considered valid in the unburnt gas zone.
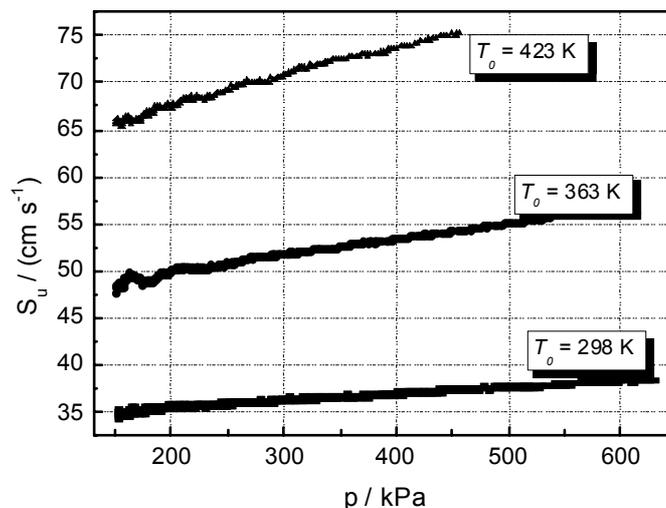

Fig. 1 – Burning velocity versus pressure during the explosion of the stoichiometric propane-air-N_2 mixture at p_0 = 100 kPa and various initial temperatures.
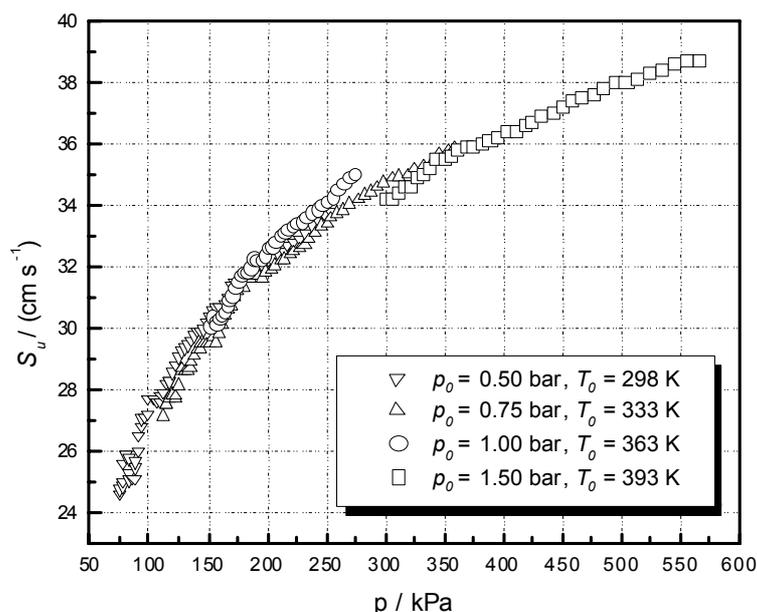
Fig. 2 – Burning velocity *versus* pressure during the explosions of the stoichiometric propane-air-CO_2 mixture at various initial pressures and temperatures.

Table 1

Thermokinetic coefficients ε of burning velocity variation against pressure in single experiments; propane-air-CO_2 mixtures

T_0 (K)	p_0 (kPa) 50	101	150	200
298	0.253 ± 0.002	0.187 ± 0.001	0.166 ± 0.001	0.153 ± 0.001
393	0.337 ± 0.003	0.245 ± 0.001	0.209 ± 0.002	0.143 ± 0.002

Following a literature suggestion, some of our measurements were made at initial pressures and temperatures chosen along the isentropes starting at 50 kPa and 298 K.[21,22] According to this procedure, burning velocities could be obtained for a pressure range from 50 to 830 kPa and a temperature range from 298 to 650 K. The isentropes $S_u(T_u)$ shown in Fig. 1 could thus be extended towards higher pressures and temperatures by choosing the adequate sets of data among measurements. A typical plot is given in Fig. 2, where four partly overlapping runs are shown. A good overlapping, especially in the early stage of runs, is a correctness proof for the proposed model. The reference burning velocity of C_3H_8-air-N_2 at ambient initial conditions is $S_{u,0} = 34$ cm s^{-1}, in good agreement with recent literature data.[23-25]

For all propane-air-inert mixtures under studied conditions, the parameters $S_{u,0}$ and ε were determined by a non-linear regression analysis. Representative values of thermokinetic coefficients are given in Table 1. The standard deviations of $S_{u,0}$ and ε are between 0.3–1.5% and 0.3–1.0%, respectively. Within examined ranges, the exponents ε exhibit a dependency on pressure and temperature. For all mixtures, ε increases with temperature and decreases with pressure.

The burning velocities of propane-air-N_2 mixtures referring to initial conditions of each experiment $S_{u,0}$ are shown as a function of pressure in Fig. 3(a) and as a function of temperature in Fig. 3(b), together with the best data fits. Similar diagrams were obtained for all examined mixtures and initial temperatures.

The data follow the expected variation of normal burning velocity *versus* pressure (at constant temperature) or *versus* temperature (at constant pressure) described by eq. (2). Choosing as reference pressure $p_{ref} = 100$ kPa, the baric coefficients (exponents) of normal burning velocities for propane-air-inert mixtures (at constant temperature) were calculated by a non-linear regression analysis of $S_u = f(p_0)$ data. Several sets of baric coefficients are given in Table 2. The thermal coefficients of normal burning velocities for propane-air-inert mixtures (at constant pressure) obtained in a similar way by choosing $T_{ref} = 298$ K are given in Table 3.
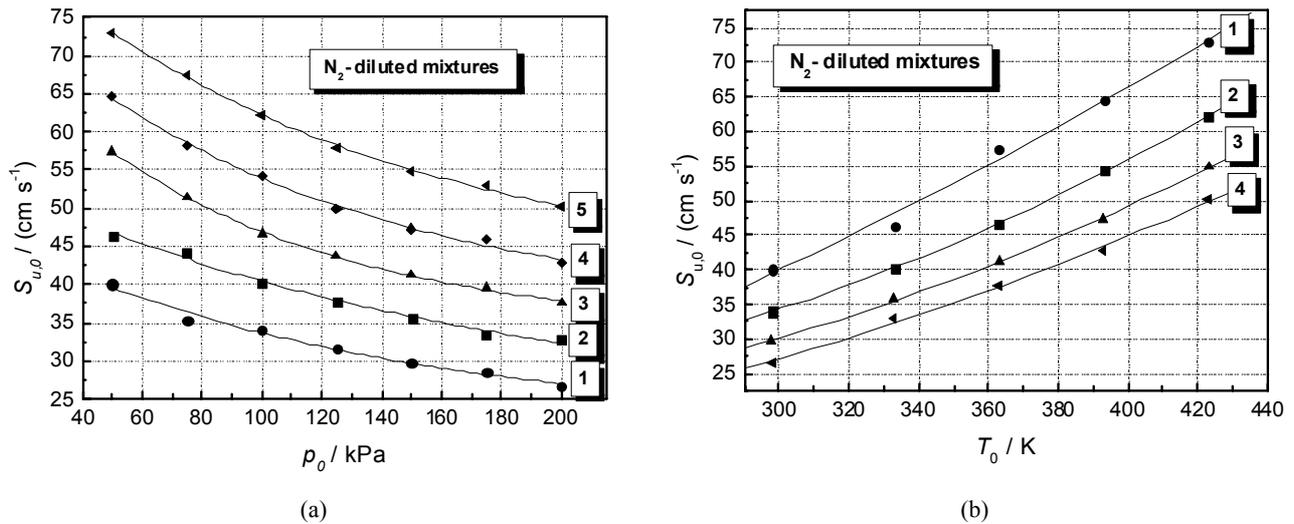
Fig. 3 – Burning velocities S_u extrapolated at the initial moment: (a) S_u *versus* initial pressure at various initial temperatures: (1) 298 K; (2) 333 K; (3) 363 K; (4) 393 K and (5) 423 K; (b) S_u *versus* initial temperature at various initial pressures (1) 50 kPa (2) 100 kPa (3) 150 kPa (4) 200 kPa.

Table 2

Baric coefficients $-\nu$ of normal burning velocities at various initial temperatures

Inert gas	T_0 (K)		
	298	363	423
Ar	0.253	0.271	0.209
N_2	0.276	0.304	0.269
CO_2	0.237	0.207	0.149

Table 3

Thermal coefficients μ of burning velocities at various initial pressures

Inert gas	p_0 (kPa)			
	50	100	150	200
Ar	1.919	2.193	2.094	2.026
N_2	1.764	1.767	1.762	1.778
CO_2	1.637	1.984	1.755	2.230

Another possibility to calculate the baric coefficient ν of burning velocities is to use the thermokinetic coefficients ε and the thermal coefficients μ using eqns. (1) and (2), when only experiments at variable initial temperature are carried out. When only experiments at variable initial pressure can be performed, the thermal coefficients μ may be calculated from ν and ε, according to a similar procedure. The thermal and the baric coefficients determined in this way have close values to those determined from burning velocities extrapolated at the initial moment. The present baric coefficients of stoichiometric propane-air-inert mixtures range well within literature data: ν = -0.17;[21] -0.13;[13] -0.25.[26] The thermal coefficient μ =1.77 of

propane-air-N_2 mixtures at p_0 = 100 kPa is lower in comparison to literature values referring to propane-air (2.13;[21] 1.83[26]), but still within the usual range of variation.

Burning velocities from kinetic modeling

The burning velocities of propane-air-inert mixtures at 300 K obtained from kinetic modeling with GRI 3.0 mechanism are plotted in Fig. 4, where a comparison between the influence of inert additives is shown: at constant inert concentration, CO_2 has the highest influence on burning velocity, followed by N_2 and Ar. In all cases, the computed burning velocities overestimate experimental

results, but their variation with the total initial pressure and the initial temperature are consistent with the variation of experimental burning velocities. Representative values of the thermal and baric coefficients of burning velocities are given in Tables 4 and 5. The baric coefficients of experimental and computed burning velocities have close values, excepting those characteristic for C_3H_8-air-CO_2, systematically lower for computed S_u. The thermal coefficients of experimental and computed burning velocities agree well for N_2- and CO_2-diluted mixtures; those referring to C_3H_8-air-Ar differ systematically, especially at higher initial pressures.

All reported data (burning velocities, baric and thermal coefficients) of propane-air-inert mixtures indicate the inert influence on propane oxidation in flames. It was widely considered that inert additives influence mostly the thermal properties of flammable mixtures, by changing their heat capacity and consequently, the flame temperature. Indeed, the burning velocities correlate well with characteristic adiabatic flame temperatures, as shown in Fig. 5 for measured data. Similar correlations are found for computed burning velocities. Inert addition influences however both thermophysical properties of the reacting mixture and the oxidation reaction kinetics. In the case of CO_2 dilution, a specific influence exists, based on its ability to dissociate and to dissipate heat by radiation.
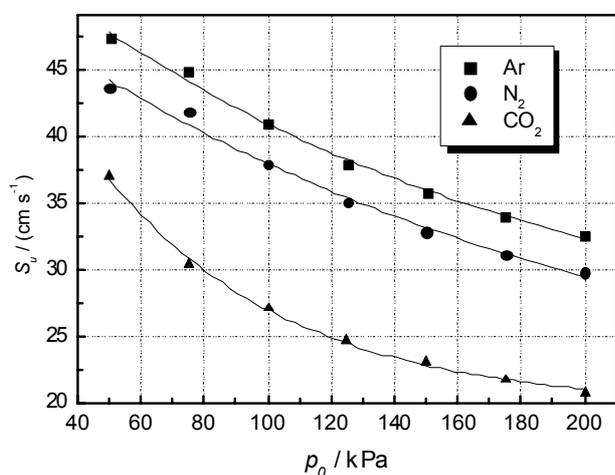

Fig. 4 – Computed burning velocities of C_3H_8-air-inert mixtures ([inert] =10 vol%) at T_0 = 300 K and various initial pressures.
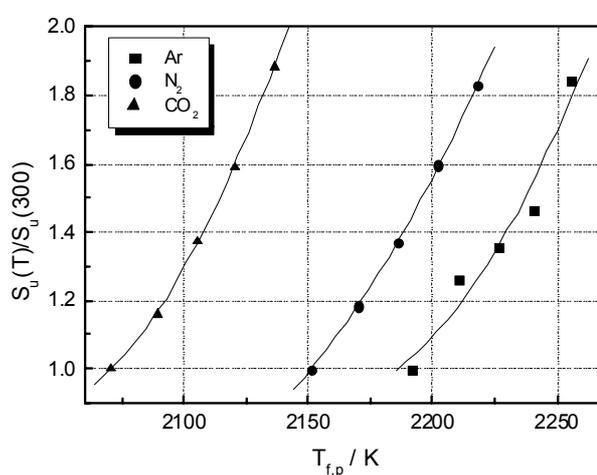
Fig. 5 – Relative burning velocities of preheated C_3H_8-air-inert mixtures at p_0 = 100 kPa.

Table 4

Baric coefficients $-\nu$ of computed burning velocities at various initial temperatures

Inert gas	T_0 (K)		
	298	363	423
Ar	0.275	0.313	0.297
N_2	0.281	0.330	0.316
CO_2	0.389	0.373	0.356

Table 5

Thermal coefficients μ of computed burning velocities at various initial pressures

Inert gas	p_0 (kPa)		
	100	150	200
Ar	1.633	1.667	1.691
N_2	1.663	1.697	1.720
CO_2	1.714	1.747	1.748

Table 6

Overall activation energies E_a (kJ mol^{-1}) of propane oxidation at various pressures, in the presence of inert gases

p_0 (kPa) Inert gas	100	200	400
Ar	347	570	544
N_2	360	458	455
CO_2	354	517	321

Table 7

Overall reaction orders *n* of propane-oxygen reaction at various initial temperatures

T_0 (K) Inert gas	298	363	423
Ar	1.49	1.46	1.58
N_2	1.45	1.39	1.46
CO_2	1.53	1.59	1.70

The overall kinetic parameters of propane-oxygen reaction

The normal burning velocity is directly influenced by the overall reaction rate in the flame front, therefore the good correlation of normal burning velocities with flame temperatures illustrated by data in Fig. 5 can be used to evaluate an overall activation energy of the combustion process. The overall activation energy of propane-oxygen reaction in the flame front of preheated propane-air-inert mixtures was calculated by a modified Arrhenius type equation:[19]

$$\ln S_u = ct - \frac{E_a}{2R\overline{T_f}} \qquad (4)$$

where $T_{fl,av}$ is the average temperature within the flame front:[28]

$$\overline{T_f} = T_0 + 0.74 \cdot (T_f - T_0) \qquad (5)$$

A typical set of data calculated from experimental burning velocities is given in Table 6.

The overall activation energies of propane-oxygen reaction in the presence of inerts determined from the experimental burning velocities at ambient pressure are within the typical values characteristic for fuel-oxidant mixtures: E_a = 385 kJ/mol for preheated ethylene-air mixtures,[29] 254 kJ/mol (for lean propane-air mixtures) or 365 kJ/mol (for the stoichiometric propane-air mixture).[30] At higher pressures, the activation energies of propane-oxygen reaction in the presence of inerts are closer to the values reported by Kuehl (E_a = 487 kJ mol^{-1}; [31]), Hill and Hung (432 kJ mol^{-1}; [13]), Zhao *et al.* (451 kJ mol^{-1};

[32]) for propane-air. Higher activation energies were determined from computed burning velocities as well, for each examined additive.

From the baric coefficients *v*, the overall reaction orders *n* can be obtained with the relationship:

$$n = 2(v+l) \qquad (6)$$

Representative values of overall reaction orders are given in Table 7. They range among reported values found for propane-air mixtures, between 1.4 and 1.8.[8,13,21] They increase slightly with initial temperature for all examined inerts, especially in propane-air-CO_2 mixtures.

CONCLUSIONS

In the present study, the flame propagation during the deflagration of stoichiometric propane/air mixtures diluted with 10% inert (N_2, Ar, CO_2) at various initial pressures and temperatures (p_0 = 30–200 kPa, T_0 = 298–423 K) in a spherical vessel with central ignition was monitored by means of pressure measurements. Using an improved relationship for the burnt mass fraction recently revalidated, the burning velocities were calculated from pressure-time records over an extended duration of spherical propagation.

In all examined conditions, propane-air-CO_2 mixtures are characterized by the lowest burning velocities in comparison with propane-air-Ar and propane-air-N_2.

The experimental burning velocities are examined in comparison to computed burning velocities, obtained from a numerical modeling of 1D laminar flames using GRI version 3.0

mechanism. For all data, the diluent influence on burning velocities is discussed. The burning velocities obtained from the detailed modeling of combustion, using the program COSILAB, have overestimated values in comparison with both the present measured velocities and with other literature data. However, a better match of computed and experimental results may be obtained by revision of input data.

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