



*Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 85th anniversary*

KINETIC MODELING OF FLAME PROPAGATION IN GASEOUS PROPANE-AIR MIXTURES

Domnina RAZUS,^{a,*} Maria MITU,^a Venera BRINZEA,^a Adina MUSUC^a and Dumitru OANCEA^b

^a "Ilie Murgulescu" Institute of Physical Chemistry, Roumanian Academy, 202 Spl. Independentei, Bucharest, Roumania

^b University of Bucharest, Faculty of Chemistry, Physical Chemistry Department, 4-12 Elisabeta Blvd., Bucharest, Roumania

Received May 27, 2011

The burning velocities, temperature and concentration profiles of various chemical species in the flame front of free laminar premixed flames propagating in propane-air gaseous mixtures were computed with the package COSILAB. Propane-air mixtures of variable composition ($[C_3H_8] = 2.5 - 6.5$ vol.%) were examined, at variable initial pressures within 0.5 and 3 bar and variable initial temperatures within 300-550 K. The modeling used the GRI reaction mechanism, developed by the Gas Research Institute-USA for natural gas-air flames in various conditions by taking into account 53 species and 325 elementary chemical reactions. The computed values of burning velocities are discussed in comparison with previously reported experimental values, derived from pressure measurements during the early stage of explosions in a spherical vessel with central ignition. The flame structure (temperature and concentration profiles across the flame front) is discussed in connection with the initial fuel concentration, temperature and pressure of flammable mixtures.

INTRODUCTION

Computational studies on one-dimensional adiabatic premixed flames were extensively used in the field of hydrocarbon oxidation kinetics, in order to determine the relative importance of various reaction steps after comparing experimental results with numerically calculated values (the normal burning velocities and the temperature and concentration profiles for various chemical species) and performing sensitivity analysis for the examined parameters.¹ Many studies were performed on lower alkane- and alkene-air mixtures, modeling the ignition/extinction of these flames or their propagation in laminar regime.²⁻¹⁴ The developed mechanisms were used also for modeling the

homogeneous self-ignition of fuel-air flames, either in jet-stirred reactors (the low-temperature regime) or in shock tubes (the high temperature regime).¹⁵⁻¹⁷

In many studies, propane was chosen as test fuel.^{2, 4-8, 10-12, 14} Indeed, propane is the smallest hydrocarbon which participates to reactions typical for larger hydrocarbons, and therefore its study affords a better understanding of the combustion mechanisms of larger hydrocarbon fuels. Most authors reported measured burning velocity together with temperature and species profiles of propane/O₂/N₂ flames stabilized usually on a flat-flame burner.¹¹ Various techniques were used to determine the burning velocities of propane in air: counter-flow flame technique,¹⁸ spherical bomb technique,^{19,20} single-jet-wall stagnation technique.²¹

* Corresponding author: drazus@icf.ro

In a previous study on flame propagation in gaseous propane-air mixtures, at ambient initial pressure and various initial temperatures we reported burning velocities from experimental pressure-time records obtained in spherically propagating flames and from a detailed modeling of laminar premixed flames,²⁰ based on the mechanism developed by Warnatz, Maas and coworkers.^{22,23} In the present work, the burning velocities of propane-air mixtures with variable initial composition, pressure and temperature from closed-vessel explosions are examined versus predicted burning velocities obtained with GRI (Gas Research Institute, USA) mechanism, widely used for modeling natural gas explosions.²⁴ Other properties obtained from computations, such as the maximum rate of heat release, the temperature and the mass fractions of molecular and radical intermediates, are examined in correlation with the initial composition, pressure and temperature of propane-air mixtures.

COMPUTING PROGRAM

Numerical simulations of propane-air flames were performed by means of the software package COSILAB version 3.0.3, developed by Rogg and Peters.²⁵ One-dimensional, premixed laminar free flames were considered, assuming the GRI mechanism, based on 53 chemical species and 325 elementary reactions (version 3.0). 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 DISCUSSION

The kinetic modeling of flame propagation in a mixture of given initial composition, pressure and temperature delivers the following results: the laminar burning velocity S_u characteristic to the stable one-dimensional (1-D) laminar, premixed free flame and data describing the flame structure: the volumetric rate of heat release, dQ/dt , the temperature and concentrations of all chemical species taken into account versus distance across the front of examined 1-D flames. Illustrative results obtained for the stoichiometric propane-air flame ($[C_3H_8] = 4.02$ vol.%) at ambient initial conditions are given in Figs. 1 and 2. The temperature profile was plotted in each graph, for a better understanding of other examined profiles, e.g. the heat release rate and the mass fractions of major chemical species.

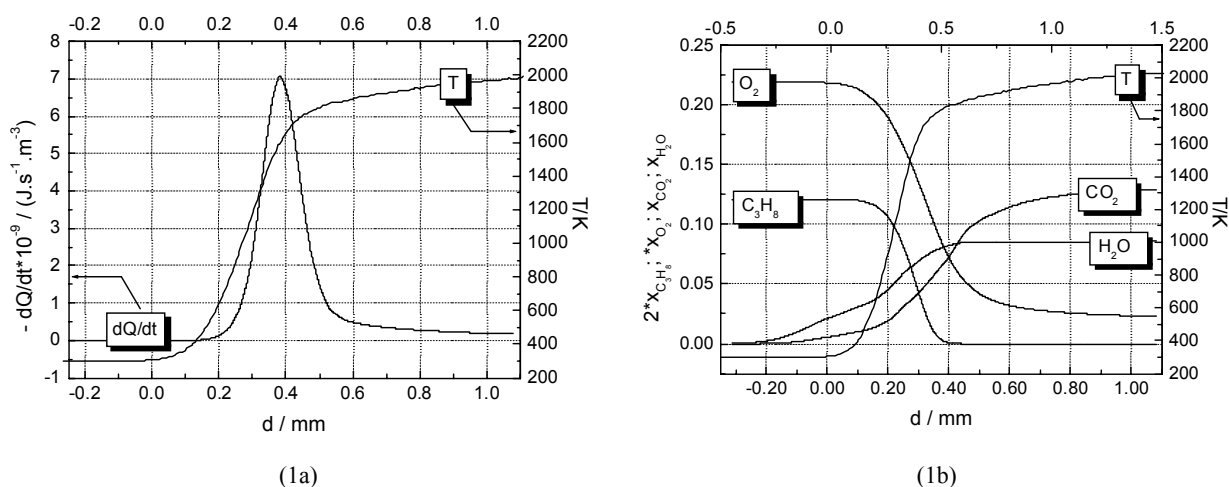


Fig. 1 – Characteristic profiles for a stoichiometric propane-air flame, propagating at $p_0 = 1$ bar and $T_0 = 300$ K: (1a) temperature and volumetric rate of heat release; (1b) temperature and mass fractions of main reactants and products.

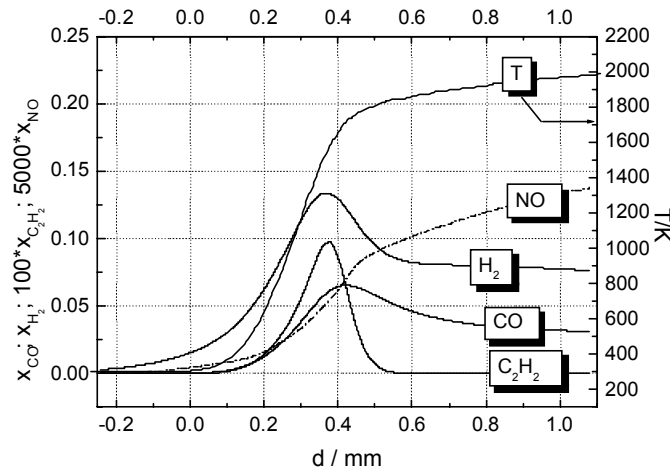


Fig. 2 – Temperature and mass fractions of molecular intermediates profiles for a stoichiometric propane-air flame, at $p_0 = 1$ bar and $T_0 = 300$ K.

The inflection point of the temperature profile T_i was considered, in early studies,²⁶ as “ignition temperature” of the premixed plane adiabatic flame. T_i divides the flame front in “the preheat zone” ($T_0 < T < T_i$) where each element of the flame front is a heat sink (the element receives, by thermal conduction, more heat from downstream hotter elements than it loses to upstream cooler elements) and “the reaction zone” ($T_i < T < T_{\max}$), where each element of the flame front is a heat source (it loses more heat than it receives). In agreement with this model, at the ignition temperature T_i the mass fractions of fuel and oxygen start decreasing and the mass fractions of main reaction products (CO_2 and H_2O) start increasing. As temperature exceeds T_i , the rate of heat release and the mass fractions of many important intermediates (CO , H_2 , C_2H_2 , HO_2 , O , H) reach peak values. Mallard and Le Châtelier considered the ignition temperature as a physical constant, characteristic to each fuel-air mixture.²⁶ The present results show that the “ignition temperature” is dependent on propane concentration and on its initial temperature and pressure; therefore, their assumption is used merely for simplified models of flame propagation.

At constant initial pressure and temperature, the profiles of flame temperature, rate of heat release and intermediate mass fractions are influenced by propane concentration. As the mixture composition approaches the lower flammability limit, all profiles are broader and flatter. A typical plot is given in Fig. 3, where temperature profiles of several lean propane-air mixtures are given. Similar results were obtained for rich propane-air

mixtures, when propane concentration increases from the stoichiometric mixture to the upper flammability limit.

The maximum value of the heat release rate, for each examined flame, is strongly dependent on initial parameters of unburned flammable mixture: composition, pressure, temperature. Typical diagrams of maximum rate of heat release computed for propane-air flames at constant initial pressure and various initial temperatures are given in Fig. 4; similar data, for propane-air flames at constant initial temperature and various initial pressures are given in Fig. 5.

The maximum value of the heat release rate for systems at ambient initial pressure and temperature, plotted against propane concentration, together with the maximum flame temperatures and normal burning velocities, are given in Fig. 6; similar data were obtained for systems at 300 K and higher initial pressures. All plots have a peak at propane concentrations ranging between 4.2 – 4.7 vol.% (range of rich fuel-air mixtures). This behavior was observed for other flammability parameters of propane-air as well: the maximum explosion pressures,²⁷ the maximum rates of pressure rise,²⁸ the adiabatic flame temperatures.²⁹ It is, in fact, a common feature of hydrocarbon-air flames, found for all properties depending on fuel concentration^{22,26} that can be associated with the rate of heat release in each flame, determined by the interplay of elementary reactions and by the variation of transport properties of gaseous mixture across the flame front as well as by the contribution of endothermic reactions.

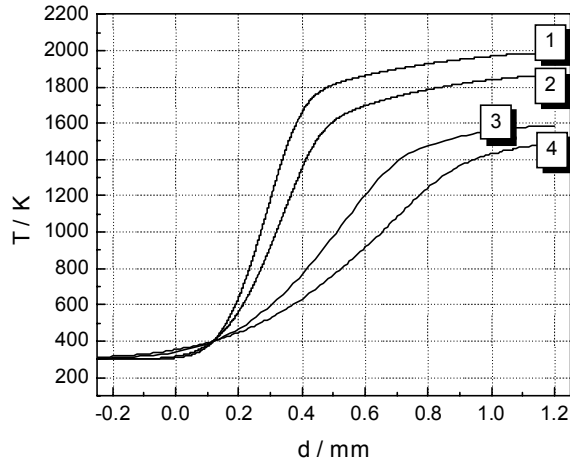


Fig. 3 – Temperature profiles of lean C_3H_8 -air flames at $p_0 = 1$ bar and $T_0 = 300$ K: (1) $[C_3H_8] = 4.03$ vol.%; (2) $[C_3H_8] = 3.05$ vol.%; (3) $[C_3H_8] = 2.46$ vol.%; (4) $[C_3H_8] = 2.26$ vol.%.

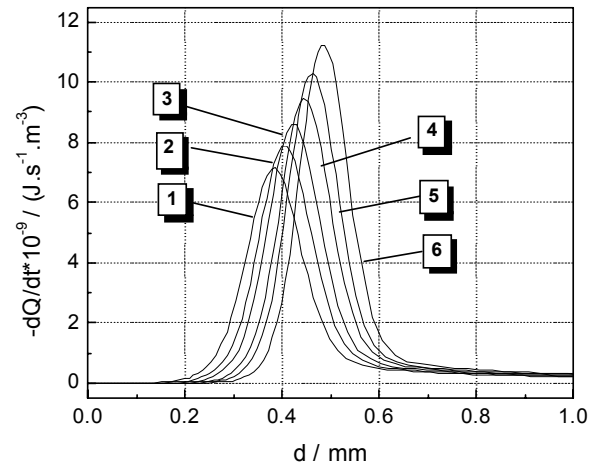


Fig. 4 – Maximum rates of heat release in the flame of a stoichiometric propane-air mixture, at $p_0 = 1$ bar and various initial temperatures: (1) 300 K; (2) 350 K; (3) 400 K; (4) 450 K; (5) 500 K; (6) 550 K.

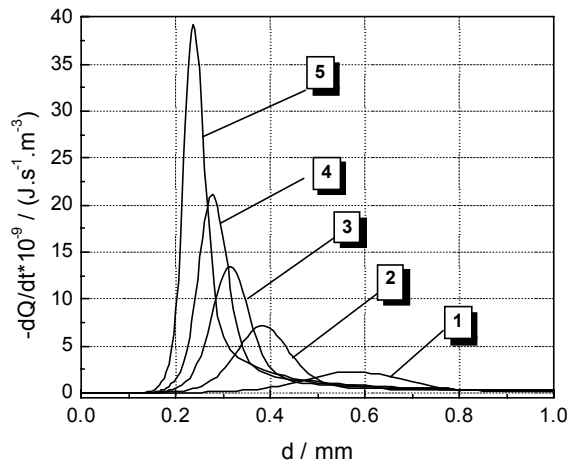


Fig. 5 – Maximum rates of heat release in the flame of a stoichiometric propane-air mixture, at $T_0 = 300$ K and various initial pressures: (1) 0.5 bar; (2) 1 bar; (3) 1.5 bar; (4) 2 bar; (5) 3 bar.

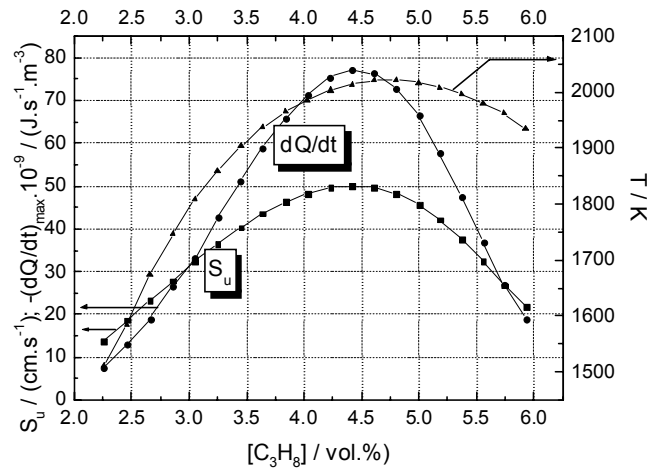


Fig. 6 – Maximum rates of heat release, flame temperatures and burning velocities of propane-air flames at $T_0 = 300$ K and $p_0 = 1$ bar.

Initial pressure, temperature and concentration influence on burning velocities are summarized in Figs. 7 and 8. In all diagrams, the burning velocities have maxima at $[C_3H_8] = 4.30 - 4.80$ vol.%.

A comparison between experimental and computed laminar burning velocities is given in Fig. 9, based on data taken from literature^{18,19,21} and including a complete set of results reported in our previous paper.²⁰ A satisfactory agreement was found between experimental burning velocities and those computed with GRI mechanism, especially in the range of rich propane-air mixtures at ambient initial conditions.

The effects of pressure and temperature on the computed burning velocity can be conveniently described by empirical equations of the power-law type:

$$S_u = S_{u,ref} \left(\frac{p}{p_{ref}} \right)^{\nu} \quad (1)$$

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

where μ and ν are the thermal and baric coefficients and $S_{u,ref}$ is the reference value of burning velocity (its value in reference conditions,

usually the ambient pressure and temperature). The results reveal a typical behavior for hydrocarbon-air flames: the decrease of burning velocities with pressure increase (the baric coefficients of computed burning velocities vary between -0.35 and -0.25) and the increase of burning velocities

when initial temperature increases (the thermal coefficients vary between 1.60 and 1.90). A comparison of baric and thermal coefficients from computed and from experimental burning velocities is given in Tables 1 and 2.

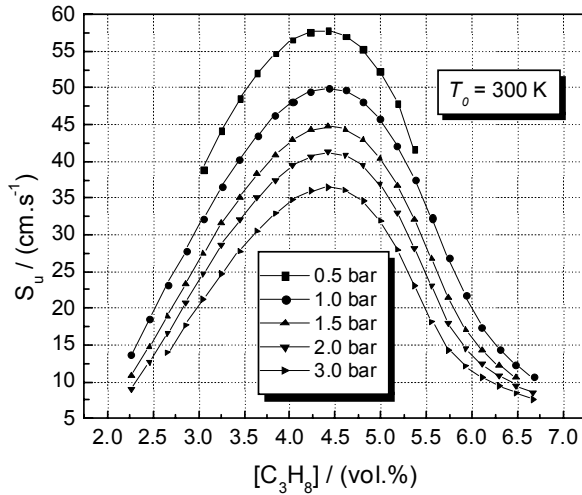


Fig. 7 – Burning velocities of propane-air mixtures at $T_0 = 300$ K and various initial pressures.

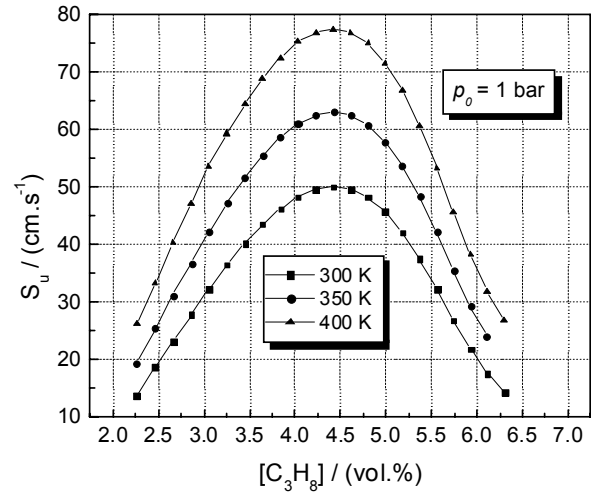


Fig. 8 – Burning velocities of propane-air mixtures at $p_0 = 1$ bar and various initial temperatures.

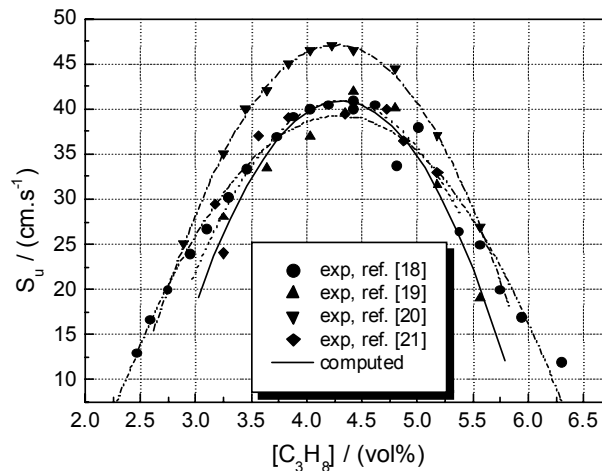


Fig. 9 – Burning velocities of C_3H_8 -air mixtures at $p_0 = 1$ bar and 300 K, obtained from experimental measurements (counter-flow twin-flame technique¹⁸, spherical vessel^{19,20} and single jet-wall stagnation flame technique²¹) and from kinetic modeling (—).

Table 1

Baric coefficients ν of normal burning velocities of propane-air mixtures at 298 K

Equivalence ratio, ϕ	Initial pressures: 0.4 – 1.3 bar	Initial pressures: 0.5 – 3 bar
	- ν , from experimental data	- ν , from computed data
0.75	0.267	0.340
0.90	0.176	0.297
1.00	0.157	0.272
1.10	0.163	0.257

Table 2

Thermal coefficients μ of normal burning velocities of propane-air mixtures at 1 bar

Equivalence ratio, ϕ	Initial temperatures: 298-430 K	Initial temperatures: 300-550 K
	μ , from experimental data	μ , from computed data
0.75	1.994	1.857
0.90	1.770	1.637
1.00	1.631	1.637
1.10	1.629	1.606

Interesting information about flame front structure is obtained from mass fraction profiles of radical intermediates. The mass fractions of radicals H, OH and HO₂ are largely influenced by the change of flame initial conditions: total initial pressure and initial temperature. Within the range of explored variation, the mass fraction of important radical species in propane-air flames decreases monotonically with pressure increase and increases monotonically with temperature increase. In turn, the change of mass fractions of

important radical species influences the normal burning velocity, a measure of overall reaction rate in the flame front.^{23, 26} Indeed, linear correlations were found between the computed burning velocity S_u and the sum of mass fractions of these species, $x_{rad} = x_H + x_{OH} + x_{HO_2}$, for flames propagating either at the same initial temperature and various initial pressures or at the same initial pressure and various initial temperatures. The results are given as regression lines for several initial conditions:

(a) data at constant initial pressure ($p_0 = 1$ bar) and variable initial temperatures:

$$\text{Lean mixture } (\phi = 0.75): S_u / (cm \cdot s^{-1}) = (3.393 \pm 0.229) \cdot 10^4 \cdot x_{rad} - (192.9 \pm 18.60) \quad (3)$$

$$\text{Stoichiometric mixture } (\phi = 1.00): S_u / (cm \cdot s^{-1}) = (3.194 \pm 0.070) \cdot 10^4 \cdot x_{rad} - (223.6 \pm 7.05) \quad (4)$$

(b) data at constant initial temperature ($T_0 = 300$ K) and variable initial pressures:

$$\text{Lean mixture } (\phi = 0.75): S_u / (cm \cdot s^{-1}) = (0.352 \pm 0.052) \cdot 10^4 \cdot x_{rad} + (8.00 \pm 2.78) \quad (5)$$

$$\text{Stoichiometric mixture } (\phi = 1.00): S_u / (cm \cdot s^{-1}) = (0.666 \pm 0.019) \cdot 10^4 \cdot x_{rad} - (7.12 \pm 1.36) \quad (6)$$

The present results prove that modeling of flame propagation is a powerful tool for characterizing the combustion of fuel-air mixtures, offering support for understanding the process under limiting conditions (laminar premixed adiabatic flames). Additional examination of flame structure (experimental measurement of concentration profiles for various species across the flame front) would validate the chosen mechanism and support its extension to higher hydrocarbons.

CONCLUSIONS

The kinetic modeling of propane-air flames, performed with COSILAB package using GRI mechanism delivered burning velocities of 1D adiabatic laminar premixed flames and profiles of heat release rate, temperature and mass fractions of molecular and radical intermediates across flame front. The computed burning velocities of propane

in air are in fair agreement with experimental values derived from pressure measurements during the early stage of explosions in a spherical vessel with central ignition or extracted from literature, for various initial compositions.

The computed burning velocities of propane-air mixtures were fitted against initial pressure and temperature of propane-air mixtures by power law equations. The thermal and baric coefficients of computed burning velocities range well among thermal and baric coefficients derived from experimental data.

The inflection point of the temperature profile T_i , named "ignition temperature", and considered in early studies as a physical constant characteristic to each fuel-air mixture of the premixed plane adiabatic flame, is significantly dependent on the fuel content and initial pressure and temperature of the mixture.

Acknowledgements: This work was supported by CNCSIS –UEFISCSU, project number PNII – IDEI code 458/2008.

REFERENCES

1. J. Simmie, *Progr. Energy Combust. Sci.*, **2003**, *29*, 599-634.
2. J. Warnatz, in "Combustion in Reactive Systems", J. R. Bowen, N. Manson, A. Oppenheim and R. Soloukhin (Eds.), Amer. Inst. Aeronautics and Astronautics Inc., 1981, vol. 76, p. 501-521.
3. F.N. Egolfopoulos, D. L. Zhu and C.K. Law, *Proc. Comb. Inst.*, **1990**, *23*, 471-478.
4. E. Djavdan, N. Darabiha, V. Giovangigli and S. M. Candel, *Comb. Sci. Technol.*, **1991**, *76*, 287-309.
5. P. Dagaut, M. Cathonnet and J. C. Boettner, *Intern J. Chem. Kin.*, **1992**, *24*, 813-837.
6. T. M. Sloane, *Comb. Sci. Technol.*, **1992**, *83*, 77-96.
7. Y. Tan, P. Dagaut, M. Cathonnet and J.C. Boettner, *Comb. Sci. Technol.*, **1994**, *103*, 133-151.
8. Z. Qin, V. V. Lissianski, H. Yang, W. C. Gardiner, S. G. Davis and H. Wang, *Proc. Comb. Inst.*, **2000**, *28*, 1663-1669.
9. F. N. Egolfopoulos and P. E. Dimotakis, *Comb. Sci. Technol.*, **2001**, *162*, 19-35.
10. Z. Zhao, "Experimental and numerical studies of burning velocities and kinetic modeling for practical and surrogate fuels", Ph.D. Dissertation, Princeton Univ. USA, 2005.
11. J. Biet, J.L. Delfau, A. Seydi and C. Vovelle, *Comb. Flame*, **2005**, *142*, 197-209.
12. C. Heghes, "C1-C4 Hydrocarbon Oxidation Mechanism", Ph.D. Dissertation, Heidelberg University, 2006.
13. A. Konnov and J. De Ruyck, Report Safekinex Project EVG1-CT-2002-00072, Vrije Univ. Brussel, 2006.
14. J. L. Delfau, J. Biet, M. Idir, L. Pillier and C. Vovelle, *Proc. Comb. Inst.*, **2007**, *31*, 357-365.
15. P. Dagaut, M. Cathonnet, J. C. Boettner and F. Gaillard, *Comb. Sci. Technol.*, **1987**, *56*, 23-63.
16. E. Ranzi, T. Faravelli, P. Gaffuri, G. C. Pennatti and A. Sogaro, *Comb. Sci. Technol.*, **1994**, *100*, 299-330.
17. D. N. Koert, W. J. Pitz, J. W. Bozzelli and N. P. Cernansky, *Proc. Comb. Inst.*, **1996**, *26*, 633-640.
18. C. Vagelopoulos, F. Egolfopoulos and C.K. Law, *Proc. Comb. Inst.*, **1994**, *25*, 1341-1347.
19. M. Metghalchi and J. Keck, *Comb. Flame* **1980**, *38*, 143-154.
20. D. Razus, V. Brinzea, M. Mitu and D. Oancea, *Energy Convers. Managem.*, **2010**, *51*, 2979-2984.
21. Z. Zhao, A. Kazakov, J. Li and F. Dryer, *Comb. Sci. Technol.*, **2004**, *176*, 1705-1723.
22. J. Warnatz, *Proc. Comb. Inst.*, **1981**, *18*, 369-384.
23. J. Warnatz, U. Maas and R. Dibble, "Combustion", Berlin, Heidelberg and New York, Springer Verlag, 3 edition, 2001.
24. G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner, Jr., V. V. Lissianski and Z. Qin, http://www.me.berkeley.edu/gri_mech/.
25. Cosilab, version 3.0.3., Rotexo-Softpredict-Cosilab GmbH & Co KG, Bad Zwischenhahn, 2009.
26. B. Lewis and G. von Elbe, *Combustion, Flames and Explosion of Gases*, Academic Press, 3rd edition, 1987.
27. D. Razus, V. Brinzea, M. Mitu and D. Oancea, *J. Hazard. Mater.*, **2010**, *174*, 548-555.
28. D. Razus, V. Brinzea, M. Mitu, C. Movileanu and D. Oancea, *J. Hazard. Mater.*, **2011**, *190*, 891-896.
29. C. Movileanu, M. Mitu, V. Brinzea, A. Musuc, M. Mocanu, D. Razus and D. Oancea, *Rev. Chim. (Bucharest)*, **2011**, *62*, 376-379.

