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Condensation flame of acetylene decomposition

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Abstract

Acetylene decomposition flame propagation was numerically analyzed and was found to be the result of the condensation reaction. Condensation processes provide reaction heat and act as a driving force for C_2H_2 flame propagation. The kinetic model reasonably predicts the level of burning velocity of the acetylene decomposition flame. The model does not demonstrate the relatively strong positive pressure dependence of burning velocity as was observed experimentally in the work of Cummings et al. [Proc. Combust. Inst. 8 (1962) 503–510]. Heat-release kinetics demonstrates a two-stage process. The first stage corresponds to heat release due to benzene formation, and the second stage of heat release corresponds to soot inception and carbonization processes. It was demonstrated that the burning velocity is sensitive to the surface growing rate constant. The use of a simplified form of presentation of the surface growing process [P.R. Lindstedt, in: Soot Formation in Combustion: Mechanisms and Models, Springer-Verlag, Berlin/New York, 1994, pp. 417–441] represents positive thermal feedback in the heat generation in a flame reaction zone.

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1. Introduction

There are a number of combustion systems with initial reactants in the gas phase and with formation of one (or several) of the products in the solid state. The mechanism of flame propagation with condensation of products in the flame reaction zone is of interest for studies of inhibited flames, CVD processes, synthesis of new materials, and sooting flames. Of special interest to this class of combustion processes is that propagation of some of these flames could be supported by the heat generated by the condensation processes. By condensation we mean formation of solid compounds from gas-phase species, molecular mass growing processes, and processes of chemical condensation and soot formation. In previous work,

we found that the high burning velocities of very lean silane mixtures, which were observed experimentally, are the result of product condensation in the flame reaction zone [1]. Condensation processes provide a relatively large heat release leading to a substantial increase in burning velocity. Another example of such a flame is the acetylene decomposition flame. Decomposition reaction is an endothermic process if we assume formation of carbon is in the gas phase (Table 1). The soot formation process provides substantial heat release thus sustaining flame propagation. Mechanisms of acetylene/air flames and acetylene decomposition at high temperatures have been discussed in a number of papers [2–6]. Major features of the combustion wave of acetylene decomposition are low burning velocity and high flame temperature [5–7]. It is of interest to note that Britton [8] observed flame propagation for ethylene decomposition for pressures higher than 30 atm and at increased initial temperatures.

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Table 1
Reaction heat (kcal/mol)

Reaction system	Products in gas phase	Solid products
$C_2H_2 = 2C + H_2$	288.4	–54.2, C (solid)
$C_2H_4 = 2C + 2H_2$	330.1	–12.5
Benzene = $6C + 3H_2$	1008	–19.8
Cyclopropene = $3C + 2H_2$	447.7	–66.2
$pC_3H_4 = 3C + 2H_2$	469.6	–44.3
1-methylcyclopropene = $4C + 3H_2$		–58.2
1-butene = $4C + 3H_2$		–39.5
1,3-butadiene = $4C + 3H_2$		–26
Methylenecyclopropane = $4C + 3H_2$		–48
Bicyclo[1.1.0]but-1(3)ene = $4C + 4H_2$		–130
3,4-dimethylenecyclobut-1-ene = $6C + 3H_2$		–80.4
Cyclopropane tris(methylene) = $6C + 3H_2$		–94.6
$SiH_4 = Si + 2H_2$	99.7	–8.3, Si (solid)
$SiH_4 + 2O_2 = SiO_2 + 2H_2O$	–200.9	–340.9, SiO_2 (solid)
$PH_3 = P + 3/2H_2$	70.2	–5.47, P (solid)
$AsH_3 = As + 3/2H_2$	51.9	–14.6, As (solid)
$SbH_3 = Sb + 3/2H_2$	29.3	–34.6, Sb (solid)
$SnH_4 = Sn + 2H_2$	33.1	–38.9, Sn (solid)
$GeH_4 = Ge + 2H_2$	67.1	–20.8, Ge (solid)
$GeH_4 + 2O_2 = GeO_2 + 2H_2O$	–161.8	–275.1, GeO_2 (solid)
$C_2H_2 = 1/3$ benzene	–47.6	
$C_2H_2 = 1/6$ acenaphthylene + $1/6H_2$	–43.9	
$C_2H_2 = 1/8$ pyrene + $3/8H_2$	–47.7	
$C_2H_2 = 1/12$ coronene + $1/2H_2$	–47.7	
$C_2H_2 = 1/16$ ovalene + $18/16H_2$	–48.4	
$C_2H_2 = 1/2$ diacetylene + $1/2H_2$	–1.31	
$C_2H_2 = 1/8 C_{16}H_2 + 7/8H_2$	–2.65	

Table 1 contains data on reaction heats of decomposition for several hydrocarbons and hydrides with solid-phase products. For comparison, reaction heats with product in the gas phase are also included. These compounds belong to the class of endothermic compounds. For comparison purposes the heats of combustion of silane and germane are also presented. Table 1 demonstrates that condensation processes contribute approximately 40% of the reaction heat for stoichiometric conditions for silane oxidation. Thus the increased range of lean flammability limits for hydrides may be the result of the contribution of condensation heat in addition to chain-branching nature of the reaction. There appear to be several reaction systems, which can support combustion due to only the chemical condensation processes. The aim of the present communication is to numerically characterize the acetylene decomposition flame as the result of condensation reactions.

2. Kinetic model and modeling procedure

Two kinetic models of acetylene decomposition were used in this work. The first was derived from the kinetic model of Appel et al. [9]. It was assumed that the inception point corresponds to pyrene formation.

Thus, the reaction flux determining pyrene formation represents the soot formation rate. For the surface growing process we used the approach suggested by Lindstedt [10]. It was assumed that the rate of the surface growing process is determined by the number of particles [10,11]. Calculations with the overall rate of soot formation (C_2H_2 and C_6H_6 were indicative species of soot inception) used in the work [11] provide approximately the same results. The influences of particle size distribution and particle/particle coagulation were not considered. The flame was assumed to be adiabatic and flame radiation was not treated in the model. The second kinetic model was a combination of the kinetic model for C_1C_2 hydrocarbon combustion [12] and a submodel [9] describing the formation of aromatic compounds. The results of calculations with these models approximately coincide except the second model leads to a somewhat higher predicted burning velocity (6.2 and 6.9 cm/s at 7 atm, respectively). For flame propagation modeling the Chemkin-2 package was used [13].

3. Results and discussion

Figure 1 shows the calculated structure of an acetylene decomposition flame. Different tempera-

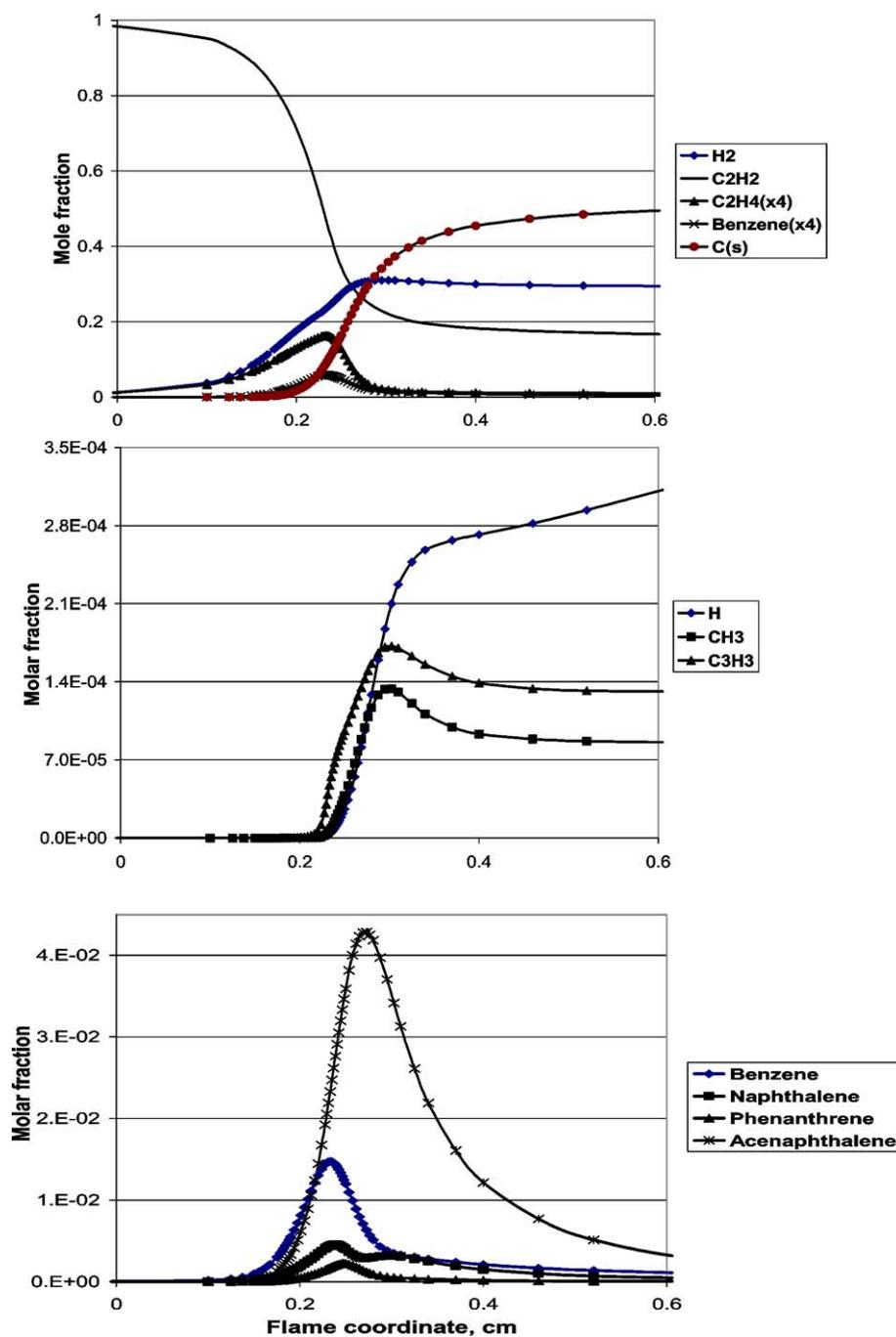


Fig. 1. Flame structure of acetylene decomposition flame (7 atm, soot amount is presented as a molar fraction of carbon atom C(s)).

tures (1900–3000 K) in the flame reaction zone can be obtained by varying the rate of the surface growing process. Flames with 2000–2400 K temperatures in the reaction zone show low levels of radical concentrations (H, CH₃) in comparison with the hydrocarbon/air flames. Increase in flame temperature leads

to substantial increase in hydrogen atom concentration and reduction in intermediate concentrations of C₂H₄, CH₄, benzene, naphthalene, and acenaphthalene. A feature of these flames is that H atom concentration does not demonstrate radical overshoot in a reaction zone. The H atom concentration con-

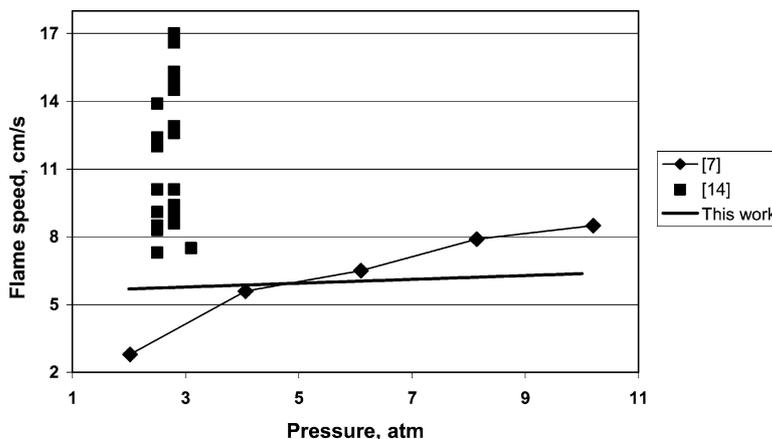


Fig. 2. Pressure dependence of burning velocity of acetylene decomposition flame. Symbols—experimental data [7,14]; line—modeling results, this work (298 K). Burning velocity measurements in [14] were performed at different initial temperatures (269–473 K).

tinues to increase in the postflame zone with the increase in temperature, depending on the degree of reaction completeness. At the same time, radical overshoot is observed for propargyl radical concentration (C_3H_3). It attains maximum concentration in the flame zone and decreases in the postflame zone. Reaction pathway analysis demonstrates that for the analyzed conditions the benzene production is dominated by propargyl radical recombination. Depending on the ratio of the surface growing process rate to the direct soot formation rate and on the level of burning velocity, incomplete acetylene decomposition in a flame reaction zone is observed. For the conditions in Fig. 1, incomplete decomposition in the flame reaction zone constitutes $\sim 12\%$ of unreacted acetylene. Incomplete consumption of acetylene in the flame reaction zone has also been observed experimentally by Cummings et al. [7].

Figure 2 illustrates pressure dependence of burning velocity. Also included are experimental data of Cummings et al. [7] and Chase et al. [14]. There is a large difference in the experimental data on burning velocity. Calculations agree reasonably with the burning velocity measurements of Cummings et al. [7]. Nevertheless the kinetic models do not account for the relatively strong pressure dependence as observed experimentally [6,7]. Analysis of the modeling results indicates a strong effect of the surface growing process on the burning velocity. The comparison of modeling and experimental data on burning velocity demonstrates that it is possible to obtain reasonable agreement by variation of the surface growing rate and its ratio to the direct soot flux. Thus the modeling of an acetylene decomposition flame and comparison with reliable experimental data can provide estimates of contributions of different processes to soot forma-

tion. It is important that the simplified form of the surface growing process [10,11] represents positive heat feedback for flame propagation. Increasing the soot surface leads to an increase in surface sites and heat generation. Thus surface growing reactions lead to positive feedback (autocatalysis) in the heat generation in a flame zone.

There are two stages of heat release in acetylene decomposition flame. The first stage is related to the benzene formation (Table 1). The second stage corresponds to inception and carbonization processes. The main portion of heat release corresponds to the benzene formation. The conversion of benzene to PAHs does not contribute much to the reaction heat (Table 1). Calculations excluding soot formation processes from the kinetic model with the pyrene as a main condensation product of acetylene decomposition lead to flame propagation with burning velocities of 1.5–3 cm/s with relatively large intermediate concentration of acenaphthalene. Flame temperature was approximately 2000 K. Acetylene decomposition flame can be considered as the consequence of the benzene formation reaction followed by PAH formation in a gas phase. Soot particles can be formed in the postflame zone and their formation may not have an influence on the decomposition flame. It is of interest that the formation of polyacetylenes will not sustain the gas-phase flame propagation due to the relatively small reaction heats (Table 1).

The kinetic models demonstrate substantial insensitivity of burning velocity to the rate constants of the models. The model that excluded soot formation and with pyrene as a flame product leads to decreases in the burning velocity and to decreased flame temperatures (~ 1800 – 2300 K), depending on the level of reaction incompleteness. Reasonable agreement with

experimental level of burning velocity can be obtained through inclusion of the soot formation process and surface growing reactions, which lead to an additional heat release. It is possible that the currently used kinetic models do not contain some important reaction(s), leading to disagreement with experimental data. We do not find reaction pathways for increasing the burning velocity except through the inclusion of soot formation and surface growing process into the model so as to provide additional (autocatalytical) heat release. A general observation from the pathway analysis is that the contribution of “overall backward processes” to the reaction process is very large, thus substantially slowing down the reaction rate of benzene formation. It is of interest to note that the propargyl–propargyl association reactions, $C_3H_3 + C_3H_3 \Rightarrow C_6H_6$ and $C_3H_3 + C_3H_3 \Rightarrow C_6H_5 + H$, represent two different types of radical reactions and can lead to different reaction behaviors. The former is the radical termination reaction, and the latter corresponds to the radical propagation reaction.

Several simplifications made in our first numerical study of the acetylene decomposition flame need to be examined in more detail in the future. We do not include in the model thermophoretic transport of soot particles, which can be important for the modeling of these flames [4,11]. For calculations of acetylene flame temperatures, the contribution of heat radiation losses is important [5–7,14]. The model does not include heat loss processes. Also, for modeling purposes it was assumed that thermodynamic properties of soot are identical to those of graphite. On the other hand, it is known that soot contains bonded hydrogen. The $[H]/[C]$ ratio depends on the conditions of soot formation and may be as large as 0.1 [15].

In this work we demonstrate that acetylene decomposition flame propagation is the result of the exothermic condensation reaction. Condensation processes provide reaction heat and act as a driving force for flame propagation (also see discussion in [6]). The kinetic models reasonably predict the level of burning velocity of the acetylene decomposition flame. Nevertheless the models do not demonstrate the relatively strong positive pressure dependence of burning velocity as observed experimentally [6,7] and which could be expected based on the observation of detonation for pure acetylene [5,16]. Heat release kinetics demonstrates a two-stage process. The first stage corresponds to heat release due to the benzene formation, and the second stage of heat release corresponds to soot inception and carbonization processes. It was demonstrated that the burning velocity is sensitive to

the surface growing rate constant. The use of simplified form of presentation of the surface growing process [10,11] represents positive thermal feedback. An increase in the number of particles and soot surface area leads to increased surface growing rate and thus to increased heat release rate.

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References

- [1] V.I. Babushok, W. Tsang, D.R. Burgess Jr., M.R. Zachariah, *Proc. Combust. Inst.* 27 (1998) 2431–2439.
- [2] H. Wang, M. Frenklach, *Combust. Flame* 110 (1997) 173–221.
- [3] J.H. Kiefer, S.S. Sidhu, R.D. Kern, K. Xie, H. Chen, L.B. Harding, *Combust. Sci. Technol.* 82 (1992) 101–130.
- [4] R.M. Fristrom, *Flame Structure and Processes*, Oxford Univ. Press, New York/Oxford, 1995.
- [5] A.I. Rozlovsky, *Basics of Fire Safety of Chemical Processes*, Khimiya, Moscow, 1983, in Russian.
- [6] B.A. Ivanov, *Physics of Acetylene Explosion*, Khimiya, Moscow, 1969, in Russian.
- [7] G.A. Cummings, A.R. Hall, R.A.M. Straker, *Proc. Combust. Inst.* 8 (1962) 503–510.
- [8] L.G. Britton, *Process Saf. Prog.* 15 (3) (1996) 128–147.
- [9] J. Appel, H. Bockhorn, M. Frenklach, *Combust. Flame* 121 (2000) 122–136.
- [10] P.R. Lindstedt, in: *Soot Formation in Combustion: Mechanisms and Models*, Springer-Verlag, Berlin/New York, 1994, pp. 417–441.
- [11] A. Beltrame, P. Porshnev, W. Merchan-Merchan, A. Saveliev, A. Fridman, L.A. Kennedy, O. Petrova, S. Zhdanoc, F. Amouri, O. Charon, *Combust. Flame* 124 (2001) 295–310.
- [12] T. Noto, V.I. Babushok, D.R. Burgess Jr., A. Hamins, W. Tsang, A. Miziolek, *Proc. Combust. Inst.* 26 (1996) 1377–1383.
- [13] R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, A Fortran computer program for modeling steady laminar one-dimensional premixed flames, Sandia National Laboratories Report, SAND85-8240, 1991.
- [14] J.D. Chase, F.J. Weinberg, *Proc. R. Soc. London A* 275 (1963) 411–430.
- [15] B.S. Haynes, H.G. Wagner, *Prog. Energy Combust. Sci.* 7 (1981) 229–273.
- [16] R.E. Duff, H.T. Knight, H.R. Wright, *J. Chem. Phys.* 22 (1954) 1618–1619.