Revue Roumaine de Chimie, **2007**, *52*(8–9), 719–724

Dedicated to Professor Victor-Emanuel Sahini on the occasion of his 80th anniversary

MODELING KINETIC LIMITATIONS OF ACETYLENE DETONATION

Mihaela PUIU, Valentin MUNTEANU and Dumitru OANCEA*

Department of Physical Chemistry, University of Bucharest, 4-12 bd. Elisabeta, 030018 Bucharest, Romania

Received April 25, 2007

Detonation and shock wave parameters for acetylene detonation were evaluated using Chapman-Jouguet and ZND models and compared to literature reported data. The discrepancies between calculated and experimental values were attributed to deviations from equilibrium hypothesis. Several subroutines containing corrective factors such as the fraction of carbon that remained uncondensed in gas-phase and heat fraction exceedingly distributed to solid phase were added to the main program to optimise the models. With these corrections, the calculated values satisfactorily agree with available experimental data.

INTRODUCTION

Acetylene is known as very sensitive to explosions, propagating as deflagrations or detonations. Due to its multiple applications in industry, acetylene was the subject of numerous studies but some aspects of its behaviour in various conditions remain unpredictable so far and the causes of reported accidents are still difficult to elucidate. The development of adequate strategies of safety and protection against explosions being a stringent nowadays requirements, the present study describes an optimized model of acetylene detonation.

During detonation, a shock wave propagates forward to energy release in the reaction zone behind it. The external parameters (specific dimensions of enclosure, roughness of walls, ignition source) impose the detonation characteristics and limits.[1,2] Among different types of detonations (one-dimensional, helicoidal, vibrating, etc.), one-dimensional detonation of pure acetylene was by far the most studied,[3] and this is the subject of our approach. Previous studies on acetylene detonation[4-6] indicated that pure acetylene leads to a stationary detonation at pressures higher than the atmospheric ones, when powerful ignition sources are used (large amounts of buster). To explain the characteristics of pure acetylene detonation, several important phenomena occurring in the detonation wave should be taken into account. A computer program was developed starting from the characteristic thermodynamic equations of detonation wave[7] and adding subroutines containing correction factors. These corrections were made in agreement with the following observed effects, reported in literature: condensation of carbon is delayed so that a certain percent remains in gaseous phase;[8] increase of carbon particles temperature in comparison to gas temperature is due to the slow heat transport between the two phases;[9] small amounts of aromatics are formed (most probably benzene);[10] 20% of acetylene remains unreacted, exceeding the equilibrium composition;[11] adiabatic coefficient of compressed products should contain the contribution of solid carbon.[12,13]

BASIC RELATIONSHIPS AND DETONATION MODELS

The evaluation of the parameters in detonation wave was accomplished using the simplest theoretical model to predict the behaviour of detonations in gases. According to the Chapman-Jouguet model[14, 15] a single Hugoniot equation is required to describe the state of the reaction products. According to Zeldovich-Neumann-Doring[7] (ZND) model, a family of Hugoniot equations is required to describe the state of the reaction products, one for each reaction extent.

The main equations necessary in the computer program are:

* Corresponding author: doan@gw-chimie.math.unibuc.ro

- Hugoniot equation:

$$\Delta e = \frac{(P_1 + P_2)\cdot(v_1 - v_2)}{2}, \qquad (1)$$

where Δe is the variation of internal energy of the mass unit; v_1 and v_2 represent the volumes of mass unit before and after the passage of shock wave, states 1 and 2, respectively; P_1 and P_2 are the corresponding pressures;

- Equation of energy conservation:

$$\Delta e = \bar{c}_V \cdot (T_2 - T_1) - \Delta e_C, \qquad (2)$$

where Δe_C is the reaction heat delivered per unity of mass and $\bar{c}_V$ is the mean specific heat of the reaction products at constant volume; T_1 and T_2 are the temperatures in states 1 and 2, respectively; this equation can be written as:

$$\bar{c}_V \cdot (T_2 - T_1) - \Delta e_C - \frac{R}{2}\cdot\left(\frac{v_1}{v_2} - 1\right)\cdot\left(n_2 T_2 + n_1 T_1 \cdot \frac{v_1}{v_2}\right) = 0, \qquad (3)$$

or

$$\frac{v_1^2}{v_2^2} - \left(1 + \frac{1}{\gamma_2}\right)\cdot\frac{v_1}{v_2} + \frac{n_1 T_1}{n_2 T_2}\cdot\frac{1}{\gamma_2} = 0. \qquad (4)$$

where R is ideal gas constant, n_1 and n_2 are the specific mole numbers in states 1 and 2, respectively, and γ_2 represents the adiabatic coefficient in state 2, $\gamma_2 = (Cp/C_v)_2$.

The equilibrium composition can be calculated using either a numerical or an analytical algorithm; the numerical algorithm is more stable and can be used even for more complex compositions. In both cases the reaction heat and equilibrium constants are calculated from the thermodynamic data given as NASA polynomials [16]. In order to calculate the detonation parameters, two models were taken into consideration:

- The model proposed by Kistiakowsky,[17] which assumes that a fraction of energy is not released due to delayed carbon condensation. The detonation parameters are calculated starting from different vaporised carbon fractions VCF;

- The model proposed by Tesner,[18] which assumes that a fraction of condensation heat accumulates on the solid particles because the resulted hydrogen is not able to maintain the thermal equilibrium. The additional increase of solid temperature due to delayed transfer of heat between the two phases is calculated by extracting a fraction from the released heat, and subsequently by adding it to solid only (1-FRQ). Other correction factors were also added: the kinetic factor KF1 – a number greater than 1 which multiplies the equilibrium constant of acetylene formation (assuming that a percent of acetylene remains unreacted, exceeding the equilibrium composition), the fraction of vaporised solid carbon VCF in excess to the equilibrium composition and the kinetic factor KF2 – a number greater than 1 which multiplies the equilibrium constant of aromatics formation (assuming that the percent of formed benzene exceeds the equilibrium composition).

The role of solid phase in acetylene detonation has not been elucidated so far. Thus, a rigorous accord between the experimental and predicted data could not be obtained. The present kinetic models, referring to the soot formation[19] (nucleation and coagulation phenomena) allow only qualitative investigations of this process.

CALCULATION METHOD AND COMPUTING PROGRAM

The input data in the used computer program are: NASA polynomials for each component, initial composition, initial temperature and pressure, calculation model of adiabatic coefficient γ_2, calculation model of equilibrium constant, fraction of released heat in gaseous phase, fraction of vaporised carbon exceeding the equilibrium composition. Since the initial state is gaseous and the final state is a heterogeneous solid-gas system, in which the solid carbon is the major component, calculation of γ_2 can be done in several ways. Due to the lack of information about the heat exchange rate between solid and gaseous phase, two other limit options were proposed: one in which c_P and c_V refer to gaseous phase compression only, and the other referring to the compression of solid-gas mixture. The obtained results show no significant differences between detonation parameters calculated with these two models. The output data contain the values of detonation parameters in Chapman-Jouguet plane: equilibrium composition, v_1/v_2,

P_1/P_2 ratios, detonation velocity D, particle velocity w and the heat correction due to incomplete decomposition of acetylene, dissociation of H_2 and vaporisation of solid carbon. Besides the detonation parameters in Chapman-Jouguet plane, the shock wave parameters are also

$$C_2H_2 \overset{K_1}{\rightleftharpoons} 2\,C_{(s)} + H_2$$
$$H_2 \overset{K_2}{\rightleftharpoons} 2\,H$$
$$C_{(s)} \overset{K_3}{\rightleftharpoons} C_g$$

The equilibrium composition can be calculated using 6 equations, obtained from the equilibrium constants K_1, K_2 ,K_3 and the balance for C, H and total mole numbers. The equilibrium constants contain the mole numbers N_j and the total pressure P. The obtained system can be solved at constant T and P, either numerically or analytically.

Calculation of detonation wave parameters

Numerical calculation started from the differential equation for isentropic compression of burned gas in Chapman-Jouguet point: $(dP/dv)_2 = -\gamma_2 \cdot P_2/v_2$

Calculation of equilibrium composition

The following equilibriums were considered:

$$(\Delta E^0_{298})_1 = 226.730 \text{ kJ/mol}$$
$$(\Delta E^0_{298})_2 = 433.416 \text{ kJ/mol}$$
$$(\Delta E^0_{298})_3 = 433.416 \text{ kJ/mol}$$

Using the following notations $\varepsilon = v_1/v_2$, $\pi = P_2/P_1$ and the ideal gas equation for states 1 and 2, respectively, one obtains:

$$\frac{P_2}{P_1} = \frac{v_1 n_2 T_2}{v_2 n_1 T_1} = \varepsilon \cdot \frac{n_2 T_2}{n_1 T_1} \tag{5}$$

and

$$\varepsilon^2 - \varepsilon\left(1 + \frac{1}{\gamma_2}\right) + \frac{n_1 R T_1}{n_2 R T_2} \cdot \frac{1}{\gamma_2} = 0 \tag{6}$$

Using equations (1), (2), (3) the detonation velocity D for the Chapman-Jouguet point [7] is derived:

$$D = v_1 \cdot \sqrt{(P_2 - P_1)\cdot(v_1 - v_2)} = \frac{v_1}{v_2} \cdot \sqrt{\gamma_2 n_2 R T_2} = \varepsilon \cdot \sqrt{\gamma_2 n_2 R T_2} \tag{7}$$

Velocity of gas behind the detonation wave w is given by:

$$w = (v_1 - v_2)\cdot\sqrt{\frac{P_2 - P_1}{v_1 - v_2}} = (v_1 - v_2)\cdot\sqrt{\gamma_2 \cdot \frac{P_2}{v_2}} = \frac{v_1 - v_2}{v_2} \cdot \sqrt{\gamma_2 n_2 R T_2} \tag{8}$$

P_1, v_1, T_1 and n_1 are known quantities, Δe_C, $\overline{C}_V$ and γ_2 can be obtained using tabulated thermodynamic data and equilibrium composition. P_2, v_2, T_2, D can be calculated by solving the system of equations (5), (6), (3) and (7), using iterative methods[6].

Calculation of shock wave parameters

Shock wave parameters are calculated starting from the stability condition of finite-thickness detonation wave [18] as it follows:

$$C^2 = D^2 = v_1 \cdot \frac{P_2 - P_1}{v_1 - v_2} \tag{9}$$

where C is the shock wave velocity;

In the front of shock wave the parameters are $\varepsilon_{SH} = v_1/v_{SH}$, $\pi_{SH} = P_{SH}/P_1$, γ_{SH} and T_{SH} calculated using ZND model. The main calculation steps are given below:

$$\varepsilon_{SH} = \frac{(\gamma_{SH} + 1)\cdot\pi_{SH} + (\gamma_{SH} - 1)}{(\gamma_{SH} - 1)\cdot\pi_{SH} + (\gamma_{SH} + 1)} \tag{10}$$

$$\pi_{SH} = \frac{\varepsilon_{SH}\cdot(\gamma_{SH} + 1) - (\gamma_{SH} - 1)}{(\gamma_{SH} + 1) - \varepsilon_{SH}\cdot(\gamma_{SH} - 1)} \tag{11}$$

The calculation begins from a presumed value of T_2 for which γ_2 is determined. At T_2 the equilibrium composition is calculated using equations 5-11. T_2, γ_2 and known amounts n_2, n_1, T_1 are introduced into equation (6) to obtain ε. The latter is introduced into equation (3) to give an improved value of T_2. The iteration continues until a small difference between two consecutive values of T_2 is reached. The final values for ε and T_2 are used in equations (5) and (7) to calculate P_2 and D; w results from equation (8).

Since γ_{SH} can be calculated only when T_{SH} is known, an iterative algorithm is required. The starting value is the temperature in Chapman-Jouguet plane. The calculation continues until a small difference between two consecutive values of T_{SH} is obtained.

Calculation of solid temperature T_s

Let q be the heat supplied to solid carbon for heating from T_2 (gas temperature) to T_s:

$$q = Q_1 \cdot [1 - FRQ] = N_S \cdot R \cdot \int_{T_2}^{T_s} C_P dT = P(T_S) - P(T_g) \quad (12)$$

where: Q_1 is the heat released by acetylene decomposition; FRQ is the fraction of heat required for gas heating; N_S mole number of solid carbon; P(T) are polynomials of type: $P(T) = a_0 + a_1 T + a_2 T^2 + ...$. One obtains:

$$P(T_s) - P(T_2) = Q_1 \cdot \frac{(1 - FRQ)}{RN_S} \quad (13)$$

The temperature of gas T_2 is known; the temperature of solid T_s is approximated using the iterative method Newton-Raphson.[6] All the calculations of detonation parameters were performed with a Basic program. Each correction factor was tested separately in order to check its weight on the model. The results were compared to available literature data.[9,11,20, 21]

RESULTS AND DISCUSSION

Influence of kinetic factor KF1 on detonation velocity and detonation temperature

The percent of acetylene exceeding the equilibrium composition was obtained varying KF1 within 1 and 6.5 (10.62- 24.46% of unreacted acetylene). The results were compared to the following experimental data:

Table 1

Reported experimental data of acetylene detonation

Ref 21	Ref 11	Ref 20	Ref 20	Ref 9
P_1 = 3 atm	P_1 = 3 atm	P_1 = 6 atm	P_1 = 3 atm	P_1 = 3 atm
	T_1 =298 K	T_1 = 298 K	T_1 = 298 K	T_1 = 298 K
T_1 = 298 K	D_{exp} = 1870m/s	D_{exp} = 1650 m/s	D_{exp} = 1560 m/s	T_{2exp} = 3500 K
% C_2H_2 = 20	T_{2exp} = 2880 K			

A reasonable agreement between experimental and calculated D and T_2 is obtained for KF1 ranging within 4.0-4.5 (20.7 – 21.6% unreacted C_2H_2). Without the correction introduced by KF1, the percent of unreacted acetylene remains 10.62%.

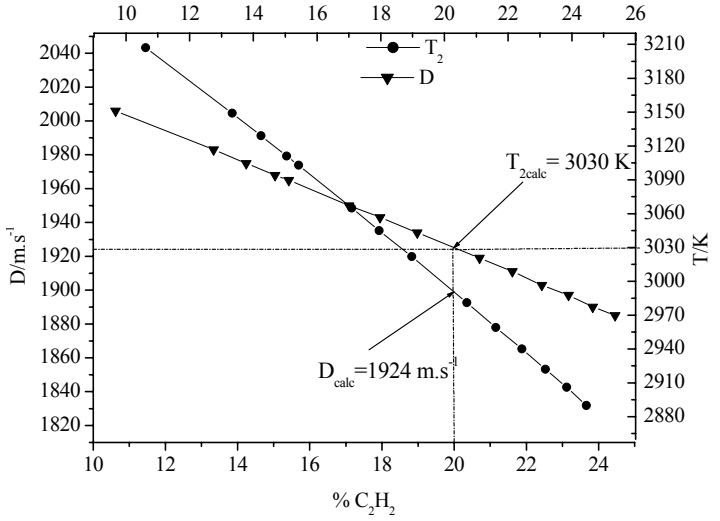

Fig. 1 – Plot of calculated detonation parameters *vs.* unreacted acetylene percent.

The calculated D and T_2 for 20% unreacted acetylene (fig.1) exceed experimental values[11] D_{exp}= 1870m/s and $T_{2\ exp}$ = 2880 K but T_2 is smaller than $T_{2\ exp}$ = 3500 K[9]. The discrepancies among the literature data are probably due to characteristics of detonation tubes. The length and diameter of detonation tubes yield different values of vaporized carbon fraction,[9, 11, 20, 21] and variation of these parameters would result in an additional difference between the values of detonation velocities.

Influence of vaporized carbon fraction VCF

Detonation temperature, shock wave temperature and detonation velocity were calculated for VCF lying within 0-0.15. The results compared to experimental sets[11, 20] are shown in figs. 2 and 3:

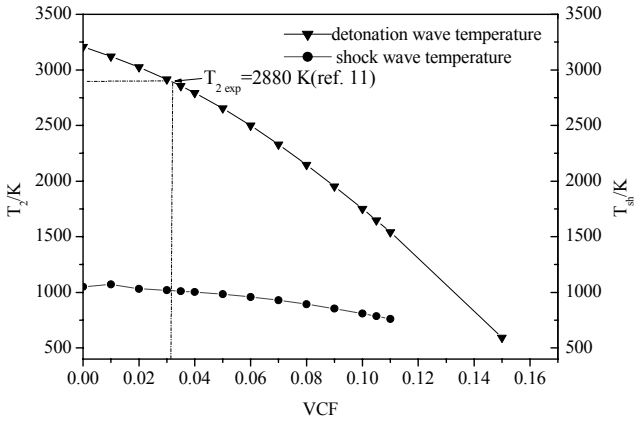

Fig. 2 – Plot of calculated T_2 and T_{sh} *vs.* VCF.

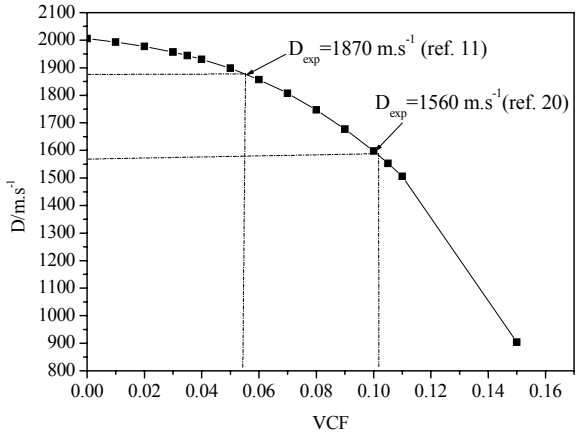

Fig. 3 – Plot of detonation velocity *vs*. VCF.

The experimental T_2 is obtained for VCF = 0.03, which can be considered an acceptable value. The literature reported detonation velocities[11, 20] are obtained for VCF = 0.054 and VCF = 0.1005, which are also possible values. Initial pressure has small effect on calculated detonation velocity; variation of pressure from 10 to 100 atm, results in very small change in detonation velocity: from 2004 to 2006 m/s.

Influence of heat fraction used for solid carbon overheating (1-FRQ)

The fraction FRQ from equilibrium reaction heat is used for gas phase, while the difference 1-FRQ goes to solid phase. It can be observed that detonation temperature T_2 decreases while the temperature of solid increases monotonously towards FRQ (fig. 4).

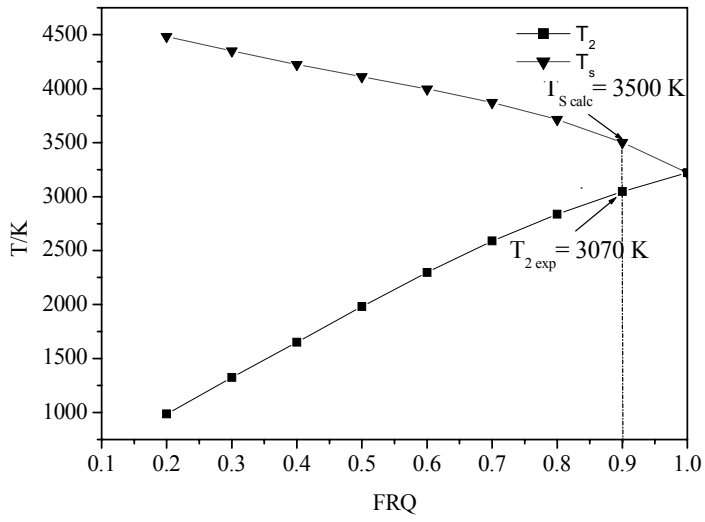

Fig. 4 – Plot of calculated solid-phase and detonation temperatures towards FRQ.

The experimental value of T_2 corresponds to FRQ = 0.9 for which the calculated temperature of solid phase[20] is 3500 K (around 200 K greater than the burned-gas temperature, a plausible hypothesis considering the mechanism of heat distribution proposed by Tesner[18]).

Influence of kinetic factor KF2

Variation of KF2 has almost no influence to the detonation parameters, since only small amounts of benzene are formed (percent of benzene ranging within 10^{-8} - 10^{-9}).

CONCLUSIONS

The corrections added to equilibrium state model are able to explain satisfactorily the discrepancies between experimental and calculated data. The percent of unreacted acetylene, the overheating of solid carbon as well as vaporised carbon fraction have significant effects on detonation parameters, leading to a reasonable agreement with literature data; the amount of aromatics produced during acetylene detonation has no significant influence on the calculated detonation parameters.

Acknowledgements: The financial support of this study by ANCS grant CEEX-ET 142/2006 is gratefully acknowledged.

REFERENCES

1. L. E. Bollinger, *ARS J.* **1961**, *31*, 588-595.
2. R. P. Lindstedt and H.J. Michels, *Comb.Flame,* **1989**, *l* (76), 169-181.
3. A. Bourlioux and A. J. Majda, *Phil.Trans. R. Soc. Lond. A*, **1995**, *350*, 29-68.
4. M. Frenklach, D. W., Clary, W. C .Gardiner and S. E. Stein, *12th Symp. Comb./Comb. Inst.*, **1969**, 887-901.
5. V. P. Korobeinikov, *Soviet Physics – Doklady*, **1968,** *12*, 1003-1005.
6. K. K. Kuo, "Principles of combustion", Wiley Interscience Publication John Wiley & Sons, 1986, p. 233-283.
7. C. L. Eisen, R. A Gross and T. J Rivilin, *Comb. Flame*, **1960**, *4*, 137-147.
8. G. N. Krikunov and A. Yu Potapov, *Fiz. Gor. Vzryva*, **1982**, *18,* 64-66.
9. V. G. Knorre and H. G. Liyakhov, *Fiz. Gor. Vzryva*, **1978**, *14* (2), 151-152.
10. A. A. Merkulov, A. A. Ovsyannikov, L. S. Polak , V. T. Popov and V. Yu. Pustilnikov, *Pl. Chem. Pl. Process.*, **1988,** *9*, 95-104.
11. R.Salut E., Duff, H. T., Knight and H. R. Wrighy, *J. Chem. Phys*., **1954**, *22*, 1618-1649.
12. B. A. Khasainov, B. S. Ermolaev, A. A. Borisov and A. I. Korotkov, *Acta Astronautica*, **1977**, *6*, 557-568.
13. M. S. Shaw and J. D. Johnson, *J. Appl. Phys*., **1987**, *62*, 2080-2085.
14. B. Lewis, G. von Elbe, *Combustion, flames and explosions of gases,* Academic Press, 1987, New York, p. 533-575.
15. G. H. Duffey, *J. Phys.Chem*., **1986**, *90*, 205-206.
16. S. H. Robertson, *Comb.Flame*, **1989**, *77*, 411-415.
17. G. B. Kistiakowsky and P.C. Mangelsdorf, *J. Chem. Phys*, **1956,** *25*, 516-519.
18. P. A. Tesner, T. D. Snegiriova, and V. G. Knorre, *Comb.Flame*, **1971**, *17*, 253-260.
19. A. V. Krestinin, *Comb. Flame*, **2000**, *121*, 513-524.
20. C.M. Cheng, *Proc. Int. Conf. on fuel-air explosions,* **1987** McGill University, Montreal , 78-82.
21. V.G. Knorre , M.S. Kopylov and P.A. Tesner, *Fiz. Gor. Vzryva*, **1974**, *13*, 863-867.