

Energy gain at pyrolysis and combustion of acetylene

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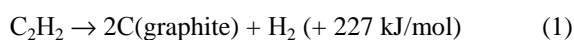
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Abstract

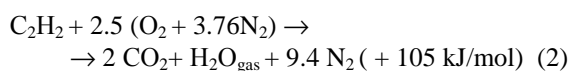
Acetylene – exothermic hydrocarbon compound. At pyrolysis of acetylene a graphitized soot and molecular hydrogen with a heat release of 227 kJ/mol are formed. In this paper the interrelation of kinetics of condensation and a heat release at the self-decomposition of acetylene behind shock waves and the usage of this heat of condensation for development of possible power cycle on the basis of detonation pyrolysis of acetylene are considered.

Introduction

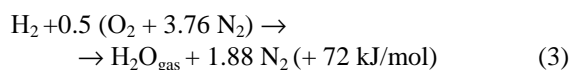
The problem of search of environmentally friendly ways of energy production becomes more and more topical. As a possible fuel for this goal acetylene could be considered, which an exothermic hydrocarbon compound is. At pyrolysis of acetylene a graphitized soot and molecular hydrogen are formed:



Owing to an essential heat release, the self-decomposition of acetylene can proceed as in a combustion mode, with the speeds from 10 to 50 cm/s, and in a detonation mode with speeds more than 2000 m/s [1-4]. It is essential that energy release at acetylene pyrolysis more than twice exceeds energy release (related to total mixture) at its combustion in air:



Moreover, as a result of reaction (1) the valuable product – soot, widely used in the industry, and hydrogen, which is the important prospective fuel, are formed. At combustion of hydrogen in air an additional energy can be obtained:



Thus, the usage of process of detonation pyrolysis of acetylene can bring an energy gain about 94 kJ/mol in comparison with its combustion in air. Additional benefits of this process are the lack of an ecologically harmful combustion product CO_2 and a yield of a large amount of soot.

To arrange a most gainful power cycle on the basis of acetylene pyrolysis, it is necessary to have a reliable data about kinetics and thermodynamics of separate stages of thermal decomposition of acetylene and the subsequent formation of the condensed carbon particles.

It is known already more than century that process of self-decomposition of acetylene can proceed in the detonation mode [2], however a question - which stages of process are responsible for the greatest energy release

and formation of a detonation wave, still was not investigated in details. From the works [1, 3, 4] it is known that detonation ability of acetylene sharply increases with growth of pressure and at compression to 60 bar acetylene explodes spontaneously at the room temperatures.

The difficulties of the analysis of this complicate nonlinear thermo-gasdynamic phenomenon are connected with existence of a large number of complex intermediate reactions of growth of the polyatomic polycyclic hydrocarbons preceding formation of the condensed carbon particles.

Thus, the purpose of this work was the analysis of interrelation of kinetics of condensation and a heat release at the self-decomposition of acetylene behind shock waves and the usage of these results for development of possible power cycle on the basis of detonation pyrolysis of acetylene.

Experimental part

The study of formation of a detonation wave of condensation in acetylene was carried out in a shock tube of a high pressure of 70-mm internal diameter with the investigation section 4.5 m long. The propagation of the reflected shock waves in the mixtures containing 10-30% C_2H_2 in Ar was investigated. Temperature and pressure behind the reflected shock wave prior to chemical transformations (the "frozen" parameters) changed over a wide range from 1300 to 2900 K and from 4 to 30 bar.

The process of shock wave propagation was registered by means of 5 pressure gauges and the time and space profiles of radiation were recorded by the ICCD camera (StreakStar II, LaVision GmbH). Besides, process of formation of the condensed particles was registered by attenuation of the probing laser radiation (extinction) on the wavelength of 633 nanometers. The detailed description of the experimental set up and the main methods of diagnostics are provided in [5].

Formation of the detonation wave of condensation

In Fig. 1 the example of ICCD camera record of time and space profile of radiation behind a shock wave in mixture of 20% of $\text{C}_2\text{H}_2 + \text{Ar}$ with various pressures is given.

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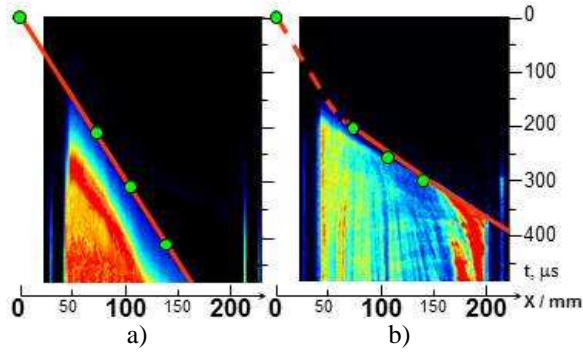


Fig.1. The time and space profiles of radiation behind shock wave in the mixture 20% $C_2H_2 + Ar$ at the “frozen” pressures and temperatures behind the reflected shock wave $P_5 = 6$ bar and $T_5 = 1580$ K (a) and $P_5 = 30$ bar and $T_5 = 1310$ K (b). Green points and red line – are the trajectory of shock wave front.

It is well seen that at initial pressure of 6 bar (see Fig. 1a) the wave of condensation which is clearly visible by intensive heating of mixture, is separated from the front of a shock wave by quite wide zone (about 50 mm) which is almost not changing over time within the area of observation. In other words, in these conditions the wave of condensation has no noticeable impact on the initiating shock wave which, continues to move with a constant speed. At increase in pressure in the same mixture up to 30 bar (Fig. 1b) the picture essentially changes – the condensation wave quickly catches up a shock wave, accelerates it and forms a detonation-like structure with the bright peak of radiation at the front.

To estimate the correlation of observed parameters of the shock waves actuated by the energy of chemical condensation of carbon vapor with the detonation parameters, the comparison of the measured velocity of a shock wave and pressure behind the front with calculations of Hugoniot adiabat curves for this mixture [6] was carried out. Results of calculations of adiabatic curves for initial mixture (curve I), and for mixture after condensation (curve II) are given in Fig. 2. Straight line 2 – 5 corresponds to the calculated velocity of the reflected shock wave. Point 6 and ray 2 – 6 presents experimentally measured peak pressure and velocity of a wave after its acceleration. Point P_{exp} shows the established pressure, and C-J point shows the parameters of a detonation of Chapman-Jouguet calculated in one-dimensional approach [6]. It is well seen that at initial pressure behind a shock wave of 30 bar the observed regime of flow is well coordinated with calculated parameters of Chapman-Jouguet.

Thus, from this consideration one can conclude that in the performed experiments with initial pressure of 30 bar the formation of a detonation wave of condensation was observed. It is important to emphasize that as the kinetics of processes of condensation cardinally differs from chain-branching mechanisms of oxidizing reactions of combustion, the mechanism of a heat release and its contribution to energy of a shock wave is

absolutely different to conventional detonation and has to be a subject of the special analysis.

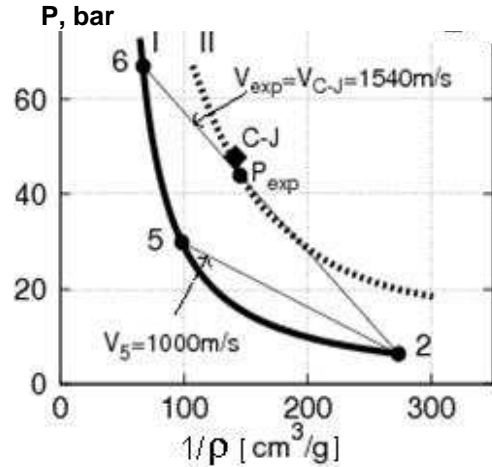


Fig.2. Hugoniot adiabat and detonation regimes for the initial mixture (curve I) and for the mixture after the condensation (curve II). Mixture: 20% $C_2H_2 + Ar$, $T_{C-J} = 2517$ K. Point 2 denotes the initial state of the mixture before the shock wave, point 5 denotes the frozen parameters behind the shock wave, point 6 denotes the peak value of the pressure behind the accelerated wave, P_{exp} is the steady-state pressure behind the shock wave, the point C-J denotes the Chapman-Jouguet parameters.

Kinetics of carbon nanoparticle condensation at pyrolysis of acetylene

The main source of information on condensation kinetics in the experiments performed are time profiles of signals of attenuation (extinction) of laser radiation I/I_0 , i.e. the relation of intensity of transmitted radiation of I to the incident intensity I_0 . Amplitude of these signals allows to find a volume fraction of the condensed phase f_V :

$$f_V = -\frac{\ln I / I_0}{\varepsilon \cdot l} \quad (4)$$

where ε – coefficient of absorption of carbon particles (for 633 nanometers ε is equal to $5.1 \cdot 10^6 \text{ m}^{-1}$ [7]), and l – absorption length (i.e. diameter of a shock tube equal 0.07 m). Time change of f_V determines two values – the induction time of the beginning of condensation τ and an effective rate constant of process of condensation k_f . In the following Fig. 3 the typical time profile of volume fraction of the condensed phase f_V in acetylene behind a shock wave is given in conditions when the heat effects owing to condensation of nanoparticles do not affect the parameters of a shock wave.

The peak at the time of passing of the shock wave front is connected with a deviation of a laser beam on density gradient. After passing of a wave the long induction time is observed. The induction time was defined as an interval between passing of the shock wave front and a point of intersection of a tangent to a

signal profile in a point of its maximum inclination with time axis. Further the sharp growth of the condensed phase follows. The rate constant of particle growth is defined by extrapolation of late stages of process by the relaxation equation

$$\frac{df_V}{dt} = k_f (f_V^\infty - f_V) \quad (5)$$

Thus, the measurements of laser extinction performed in all series of experiments allowed to extract the most important kinetic characteristics of the process of formation of the condensed carbon particles – the induction time τ and the effective rate constant of particle growth k_f in the studied conditions.

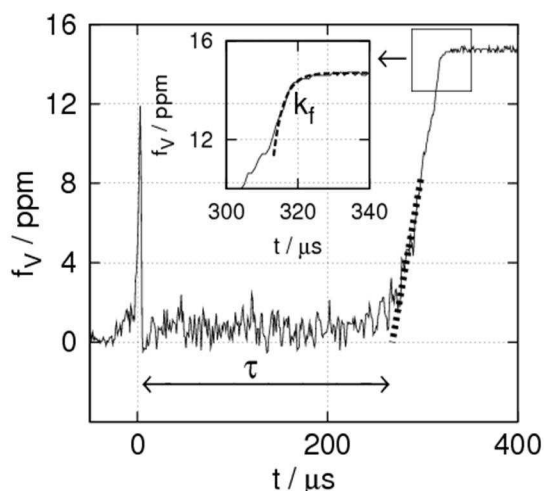


Fig.3. Typical time profile of a volume fraction of the condensed carbon determined by the signal of attenuation of the probing laser radiation (see (4)) in the pyrolysis of C_2H_2 behind the shock wave in the mixture 20% C_2H_2 +Ar and results of its processing. The temperature and pressure behind the shock wave comprise 1562 K and 6.21 bar.

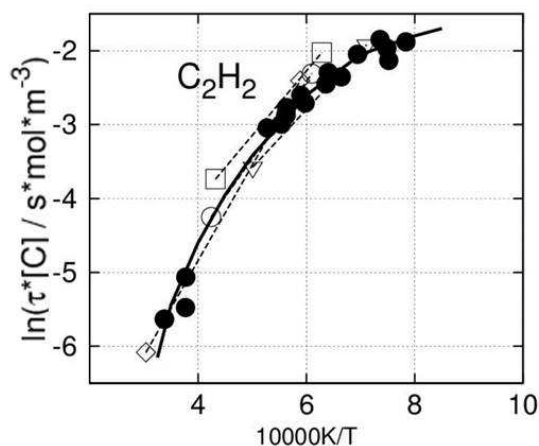


Fig.4. The induction times of particle formation in comparison with the previous data: \square - 5% C_2H_2 , [8]; \circ - (0.2-1%) C_2H_2 , [9]; ∇ - 2% C_2H_2 , [10]; \diamond - 10% C_2H_2 , [11].

In Fig. 4 the dependences of the induction time on the "frozen" temperature T_5 behind the reflected shock wave in the studied mixtures are presented. Note that τ being the phenomenological characteristic of process and it cannot be directly attributed to any specific chemical reaction during pyrolysis.

It is well seen that data on the induction time in the mixtures containing 10-30% of C_2H_2 well agree with the data of the previous measurements obtained in much more diluted mixtures.

In the following Fig. 5 data on the rate constants of particle growth are given. One can see that, unlike the induction time, values of k_f measured in this work, significantly differ from results of the measurements obtained in highly diluted mixes. Notable that the data measured in the mixtures containing (10 - 30)% C_2H_2 differ from diluted mixtures (less 3% C_2H_2) more than an order of magnitude.

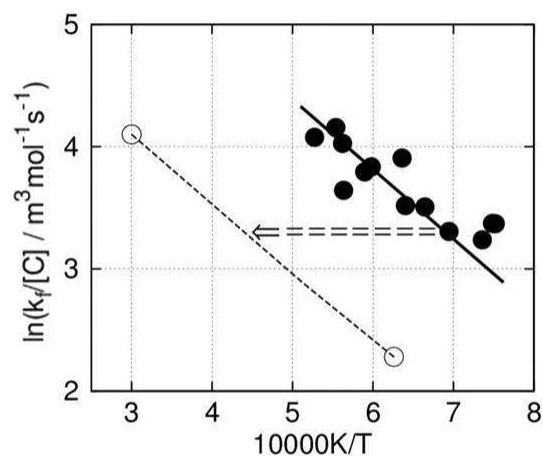
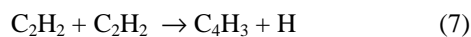


Fig.5. Rate constant of particle growth in comparison with the previous data for highly diluted mixtures. \bullet - 20-30 % C_2H_2 (this work), \circ - (0.2-1%) C_2H_2 [9].

In the analysis of the obtained data it is important to mean that acetylene pyrolysis, just as any other hydrocarbons, does not form directly the carbon clusters. For example, in work [12] as primary reactions of pyrolysis of acetylene reactions of abstraction of H atom :



or polymerization of C_2H_2



under various conditions of pyrolysis are considered. During further reactions the complex hydrocarbon radicals form either poly-acetylene [13, 14], or polyaromatic structures [14, 15].

In any case, the complex hydrocarbon molecules which are formed at these stages of process, most probably are transparent for the probing laser on 633 nanometers, and exactly this stage reflects the long induction time in acetylene mixtures. As the measured induction times in these experiments related to the "frozen" T_5 temperature well coincide with data for the

diluted mixtures (see Fig. 4), it is possible to draw a conclusion that the heat release at these stages of process is not essential yet, and temperature of the mixture does not differ noticeably from initial T_5 values.

The further stages of process which are characterized by formation of the carbon particles non-transparent for 633 nanometers, specify on considerable discrepancy of the measured values of rate constants of condensation with data of the previous works (see Fig. 5). It is most natural to assume that observed distinction of particle growth rates with the diluted mixtures is caused by an essential heat release at this stage of the process leading to increase of temperature. The simple evaluations based on integrated thermal effect of reaction (1) show that growth of temperature can reach more than 800 - 1000 K. Arrow in Fig. 6 shows the shift of the obtained k_f values as a result of increase in real temperature of mixture. One can see that these values are coordinated with data of measurements in diluted mixtures.

It is usually supposed that the growing polycyclic hydrocarbons, gradually losing hydrogen atoms, gain properties of carbon particles at a ratio between number of hydrogen N_H and carbon N_C atoms in a particle of $N_H/N_C < 0.1$ and $N_C > 10^3$. At these particle sizes an essential increase in their refractive index takes place which is manifested by the sharp growth of an extinction on $\lambda = 633$ nanometers.

Thus, based on obtained data it is possible to draw a conclusion that the main reason of difficulty of process of formation of a detonation wave in acetylene at low pressures consists in the long induction time, which is not accompanied by the noticeable heat release. Really, the products of disintegration of C_2H_2 are the hydrocarbon radicals which start being polymerized, but do not form carbon particles [15]. This stage of process spatially separated the front of a shock wave and a zone of condensation, thus, interfering with influence of hot layers of mixture on parameters of a shock wave. The increase in pressure and, respectively, concentration of the reacting particles leads to narrowing of this zone and the accelerating of its heating up by a zone of the heat release. The subsequent growth of temperature causes a sharp reduction of induction time (see a solid curve in Fig. 4), and collapse of all process with formation of a detonation wave.

To the possibility of use of energy of detonation pyrolysis of acetylene

The essential heat release characterizing detonation pyrolysis of acetylene and lack of carbon dioxide emission creates very favorable background for the organization of an environmentally friendly and effective power cycle.

In 1940 Ya.B. Zeldovich [16] showed that the most favorable in energy sense is the cycle using transformation of chemical energy of fuel by means of a detonation wave.

Recently the investigations of possibility of use of a frequency gas detonation for creation of the jet engines working both in rocket and in the propulsion jet mode are actively carried out. Advantages of the pulse

detonation engine (PDE) consist not only in use of fuel combustion in an effective thermodynamic cycle, but also in simplicity of a design. Model PDE represents a tube, one end of which is closed, and another is open. In the rocket mode (with an oxidizer onboard) the tube is equipped with systems of initiation and supply of gas mixture, in the propulsion jet mode the effective diffusers are used, which are necessary for an air intake. In any mode after filling of a tube with gas mixture, the initiation of a detonation is carried out. The detonation wave creates an elevated pressure on the closed end of a tube (a traction wall), products of a detonation expire through the open end (nozzle), then the tube is again filled and process repeats.

Ability of acetylene to oxygen-free decomposition with formation of a detonation wave of condensation and release of 227 kJ/mol energy can provide a high specific impulse of PDE working both in rocket and in the propulsion jet mode.

Conclusions

As a result of the performed experiments it is revealed that the main heat release determining positive integrated energy balance of detonation pyrolysis of acetylene occurs at a stage of formation and growth of the condensed carbon nanoparticles. On the basis of the analysis of the obtained data the possibility of control of processes of pyrolysis of acetylene is shown.

The principles of the new environmentally friendly power cycle allowing to obtain thermal and kinetic energy without use of oxygen and formation of carbon dioxide on the basis of detonation pyrolysis of acetylene are formulated.

Acknowledgements

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