Soot formation, structure and yield at pyrolysis of gaseous hydrocabons behind reflected shock waves

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Summary. Laser radiation absorption and emission techniques are used to study the kinetics of formation, yield and structure of soot at pyrolysis of methane, acetylene and propane behind the reflected shock waves over the temperature range 1600 - 4000 K. Temperature dependencies for the induction time of soot condensation and yield are obtained from experimental measurements. Analysis of microphotos and electron photographs of carbon materials has shown that fine-dispersed graphite is the main component of their structure over the investigated range of parameters.

1 Introduction

Shock tubes are frequently used for pyrolysis studies, since they permit synthesizing different substances from gas mixtures over a wide range of temperatures and pressures [1–3]. There are many works, in which pyrolysis is considered along with the oxidation process [4,5]. The presence of oxygen exerts an essential influence on the kinetics of chemical reactions, at the same time shifting considered processes into a lower temperature region. In our case, the consideration of the pyrolysis without the oxygen participation makes it possible to investigate it only under pure thermal excitation conditions, which requires higher initial temperatures. The objective of the present work was to investigate the soot formation, structure and yield at the pyrolysis of methane, acetylene, and propane within a wide range of post-shock temperatures.

2 Experimental setup

The square shock tube of 4.5 m long has been applied for these studies (fig. 1). The gas emission behind the reflected shock wave was registered at two wavelengths corresponding to the radiation of the C_2 ($\lambda = 517\ nm$, $\Delta = 5\ nm$) and CH radicals ($\lambda = 430.8$ nm , $\Delta = 2.5\ nm$). Emissions were detected by interference filters and recorded by photomultipliers. An attenuation signal of laser radiation was recorded by a photoresistor in combination with narrow-band interference filters ($\lambda_1 = 632.2\ nm$, $\lambda_2 = 632.8\ nm$, $\Delta\lambda_2 = 2.6\ nm$) and optical glasses ($KC$-10, KC-13) that used for cutting off a parasitic spectrum caused by gas self-emission at high temperatures.

Since the measuring gas volumes behind the reflected shock wave during observations of the laser absorption and gas emissions were equivalent, the instant of the luminosity peak was chosen as a reference time for measurements of laser absorption coefficients. This criterion corresponded to the maximum of production of C_2 and CH radicals during pyrolysis. The concentration of condensed soot $[C_{soot}]$ was calculated by means of Lambert-Beer's law.

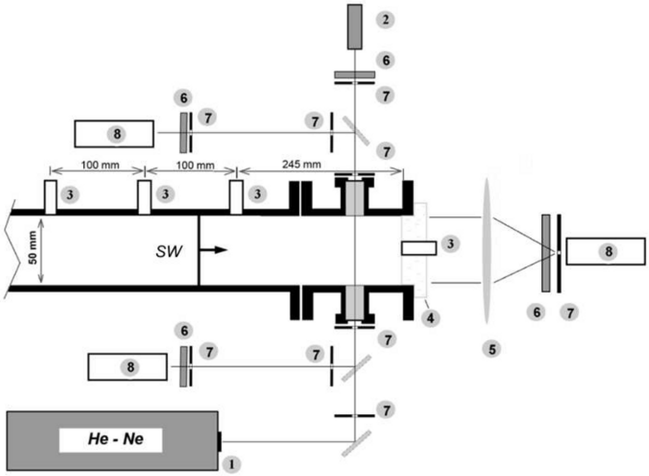

Fig. 1. Test section of the shock tube and the optical setup for pyrolysis studies behind the reflected shock wave. 1 - He-Ne laser; 2 - photoresistor; 3 - pressure sensor; 4 - transparent end wall; 5 - lens; 6 - interference filters; 7 - diaphragm; 8 - photomultipliers.

3 Result

Figs. 2,3 plots obtained temperature dependencies for the induction time of soot condensation and yield at pyrolysis of acetylene and propane behind the reflected shock wave. It is seen that the temperature dependence of soot yield for propane similar to acetylene [1, 2] has a typical "bell-shaped" form. However, a maximal soot yield in propane is located at higher temperatures $2400 - 2800\ K$, and in comparison with the acetylene its profile is essentially broadened.

For the most characteristic parts of the soot yield plots,an analysis of soot fraction microphotos and electron photographs has not revealed the existence of fullerenes and nanotubes in sample materials. It is found that fine-dispersed graphite is the main component of the soot structure at the studied range of pressures and temperatures.

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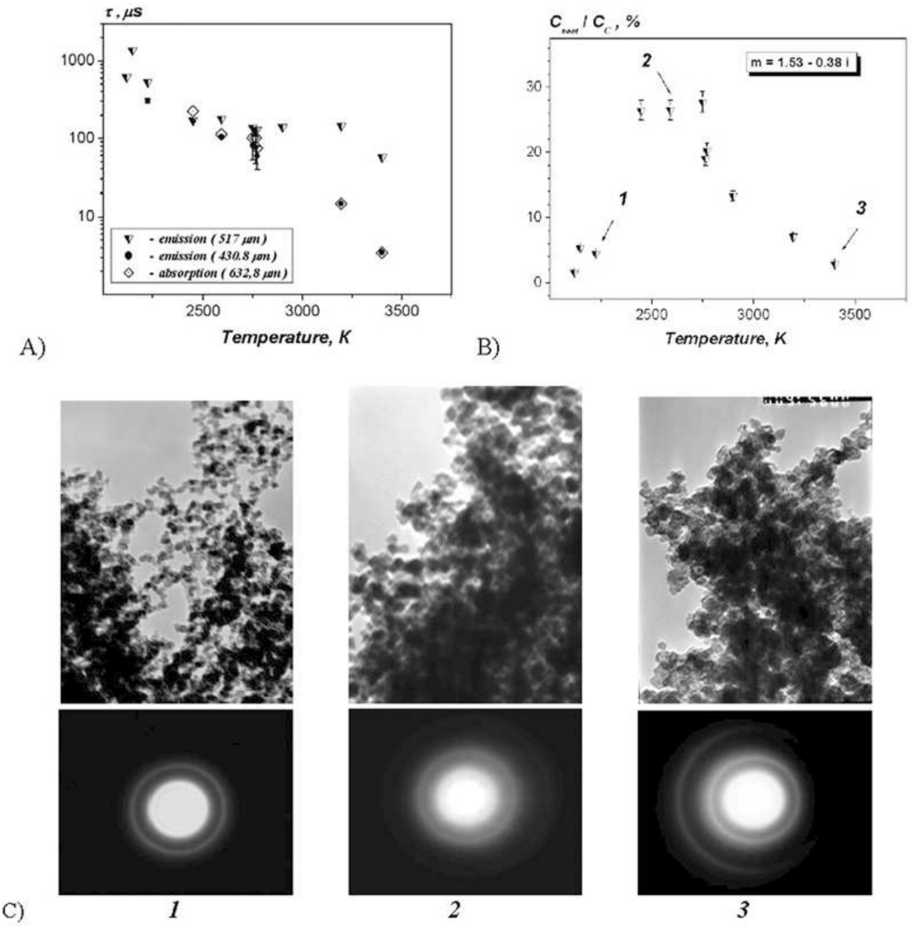

Fig. 2. Induction time (A) and soot yield (B) vs. gas temperature behind the reflected shock wave in C_3H_8/r (4:96) mixture and the microphotos and electron photographs of carbon materials at parts of the dependence (B) during pyrolysis: 1 - 2224 K; 2 - 2590 K; 3 - 3399 K

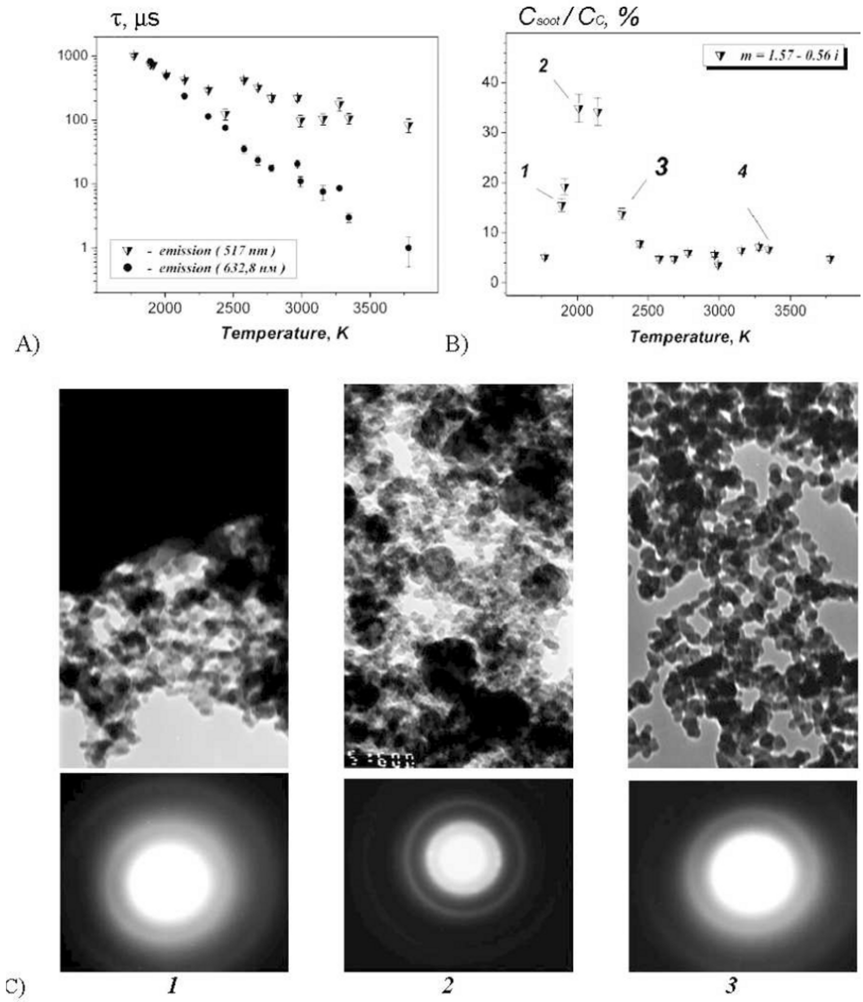

Fig. 3. Induction time (A) and soot yield (B) vs. gas temperature behind the reflected shock wave in C_2H_2/Ar (2:98) mixture and the microphotos and electron photographs of carbon materials at parts of the dependence (B) during pyrolysis: 1 - 1852 K; 2 - 2010 K; 3 - 3277 K;