



# Experimental study of temperature influence on carbon particle formation in shock wave pyrolysis of benzene and benzene–ethanol mixtures



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## ABSTRACT

The carbon particle formation process in a pyrolysis of benzene and benzene–ethanol mixtures diluted by argon at initial temperatures 1650–2600 K and pressures 1.4–5.5 bar behind reflected shock waves was studied. The manifold optical diagnostics: emission–absorption spectroscopy for gas–particle temperature, time-resolved laser-induced incandescence (Ti-Re LII) for particle size evaluation and laser light extinction for the volume fraction of condensed phase measurements were applied simultaneously. The temperature in pyrolysis process was found to differ significantly from the initial temperature behind the reflected shock wave in all studied mixtures. The real temperature dependences of volume fraction of condensed phase at the wavelength of 633 nm and particle size based on the performed measurements were specified and analyzed. The effect of ethanol addition on carbon particle formation and reaction temperature in benzene pyrolysis is discussed.

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## 1. Introduction

One of the major problems in combustion is the reduction of particulate carbon emission. The key point to study this problem is the investigation of the processes of condensed carbon particle formation. It is generally known that carbon particles, usually attributed to soot, have a core consisting of polyaromatic hydrocarbons (PAH). Benzene molecule represents a first aromatic ring and it is considered as one of the initial steps towards PAH growth [1].

The reactive temperature is crucial parameter for soot formation process. The well-known bell-shaped temperature dependences of soot yield and the particle size were observed in shock wave pyrolysis and flames [2,3]. In benzene the shift of about 200 K of the top of bell-shaped temperature dependence of soot yield towards higher temperatures was found with increasing of benzene concentration from 0.5% to 2% [2], the shift to the lower temperature was observed in pyrolysis of 0.5–1.5% toluene in argon [4]. However there is no kinetic reason for the change in temperature dependence of the soot yield with varying initial hydrocarbon concentration. Note that the reaction temperature

in majority of shock tube studies was assumed equal to the initial temperature behind the front of the reflected shock wave (so-called frozen temperature) due to high dilution in bath gas. In [3] it was supposed that the reason of the apparent change of bell-shaped curve position is the difference of the reaction temperature from the frozen temperature due to heat consumption or release at the initial steps of pyrolysis. The difference of the reaction temperature at shock wave pyrolysis of ethylene from its initial value behind the front of shock wave was predicted in [5]; besides that similar effect was experimentally observed in pyrolysis of carbon suboxide [6], acetylene, n-hexane, and benzene [7]. Therefore the correct determination of the real temperature during soot formation process could impact not only on the rates of chemical reactions, but also on the interpretation of the measurements of carbon particle yield under various conditions.

The oxygenated additions are expected to decrease a condensed carbon formation. Ethanol is widely produced from biomass and it is a promising substance as an additive to the fuels. The suppression effect of 0.31% of ethanol addition on PAH and soot formation was found in a shock wave pyrolysis of 0.31% benzene in argon [8] and in premixed fuel-rich ethylene–air flames by addition ethanol of 5% and 10% in oxygen by weight in the fuel [9]. In these studies the essential inhibition effect was explained by the increase of oxidation rate of carbon particles and their precursors. Another route of suppression effect of ethanol additives is the formation

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of H<sub>2</sub>O after decomposition of ethanol and consequent consumption of hydrogen atoms, that promote HACA mechanism of surface growth of carbon particles, with production of OH and H<sub>2</sub> [8]. On the other hand, a small amount – 10% replacement of benzene by oxygenated additives (MTBE, methanol, ethanol, isobutene) can promote the carbon particle formation due to peculiarity of the kinetics of blend pyrolysis [10]. The experimental study [4] showed an increase of soot amount in shock tube pyrolysis of 1% toluene + (1–3)% ethanol mixtures. The increase of carbon particle yield with 2–9% replacement of ethylene by ethanol in non-premixed ethylene flame was observed in [11]. These results are in conflict with suppression effect of ethanol admixture in shock tubes [8] where the decomposition of initial hydrocarbon occurs due to pyrolysis process that is similar to non-premixed flame conditions. Besides the uncertainty in the mechanism of ethanol suppression effect on carbon particle yield, no attention was paid to the reaction temperature influence on the pyrolysis of hydrocarbon–ethanol mixtures.

The present study was focused on the actual temperature behavior and the resulting temperature influence on the carbon particle formation process during pyrolysis of (1–2)% benzene and 1% benzene + (1–3)% ethanol diluted in argon. The main merit of this study is the simultaneous measurements of carbon particle size, volume fraction and current reaction temperature.

## 2. Experimental methods

### 2.1. Shock tube

The experiments were performed behind reflected shock waves in a conventional diaphragm type shock tube with an inner diameter of 50 mm (Fig. 1). After the each experiment the shock tube has been cleaned by alcohol to remove the water from the shock tube walls. The shock tube was evacuated down to the pressure of 10<sup>-2</sup> Torr by a fore-vacuum pump before every run. The test gas mixtures were prepared manometrically in a mixing vessel. The gases with the purity of 99.9% for benzene, 99.999% for argon and 95% water solution of ethanol were used. In case of benzene and ethanol the saturated vapors for mixture compounding at room temperature without extra heating were used. The blends were kept in mixing vessel for at least an hour before the experiment. The investigated mixtures and ranges of experimental conditions are listed in Table 1. The data of each shock tube experiment are listed in supplement material #1. The initial temperature  $T_5$  and the pressure  $P_5$  behind the front of the reflected shock wave were determined based on measured incident shock wave velocity by applying one-dimensional gas-dynamic theory with the assumption of “frozen” reaction conditions. An inaccuracy of the temperature  $T_5$  calculation was about 1–1.5% for all range of experiments and was caused by an uncertainty of incident shock wave velocity measured by three pressure transducers. The optical access to the measurement section was given by four calcium fluoride windows of 6 mm in a diameter, mounted perpendicular to each other at the distance of 45 mm from end flange of the shock tube.

### 2.2. Gas-particle temperature measurements

The emission–absorption spectroscopy was applied for the time-resolved temperature measurements during the pyrolysis of hydrocarbons. This method is based on simultaneous detection of emission and absorption of reactive mixture at the same wavelength [12]. The measurements were carried out by two identical optical channels that focus the light from the probe region via the pair of the calcium fluoride windows installed in a horizontal plane of the shock tube and further via lenses onto two photomul-

tipliers (Fig. 1b). The first channel registered an emission only. The second channel was exposed to radiation from reference source with known brightness temperature. Thus the second channel detected the combination of absorption and emission of reaction mixture. The optical arrangement allowed changing the channels to check their volume identity. The diaphragm at Fig. 1b had two holes. When both holes are opened and light reference source is turned on, both detectors measure the combination of absorption and emission. When light reference source is turned off, both detectors measure emission only. During the experiment only one hole is opened.

Taking into account Lambert–Beer’s and Kirchoff’s laws one can get the following expression for the temperature determination:

$$T(t) = \frac{hc}{\lambda k} \left\{ \ln \left[ 1 + \left( e^{\frac{h}{\lambda k T_0}} - 1 \right) \left( 1 - \frac{I_a(t) - I_0}{I_e(t)} \right) \right] \right\}^{-1} \quad (1)$$

here  $I_e(t)$  and  $I_a(t)$  – are the intensity of time-resolved emission and absorption + emission respectively,  $h$  – is the Planck constant,  $c$  – is the speed of light,  $k$  – is the Boltzmann constant,  $\lambda$  – is a diagnostic wavelength,  $T_0$  – is the brightness temperature of the reference source and  $I_0$  – is the initial intensity of radiation of the reference source.

The main advantage of this temperature measurement technique is that it requires only a calibrated light source, without knowledge of either optical properties of observable reaction mixture or the spectral sensitivity of the detection system. The tungsten ribbon lamp was used as the reference source for absorption channel. The wavelength of 589 nm (centered using a band pass filter with FWHM 20 nm) corresponding to sodium D-line was chosen in order to measure the gas temperature before the condensed phase appearance. The sodium atoms are the inherent natural impurity in argon. Unfortunately, owing to quite low temperatures and insufficient sensitivity of the detection system the emission/absorption signals from sodium atoms were inappropriate for reliable measurements in the most experiments. Thereby the temperature measurements started at the times of appearance of the condensed particles that absorb and emit well in the visible range of spectrum. The carbon particles are assumed to be in the thermal equilibrium with the surrounding gas since the characteristic time needed for the thermal relaxation of nanoparticles with sizes of up to 100 nm with the surrounding gas at atmospheric pressure is less than 1  $\mu$ s [13]. The time resolution of the detection system was about 10  $\mu$ s, the space resolution was 3 mm. In Fig. 2 the example of measured emission/absorption signals (a) and corresponding calculated temperature time profile (b) are presented. In Fig. 2 the time scale goes with incident shock wave arrival, however, the working conditions are achieved only behind the reflected shock wave so below for all the data presented time scale goes starting from the moment of reflected shock wave arrival. The time interval applicable for the measurements was confined by gas-dynamic perturbation and varied with the incident shock wave velocity. The minimal time accessible for measurements among all the range of investigated conditions was equal to 700  $\mu$ s. The error of measurements depended on the signal-to-noise ratio and the difference between the temperature of reactive mixture and the brightness temperature of reference source  $T_0$ . The value of  $T_0$  was varied in the range of 1970–2260 K. The total error of temperature measurements was amounted to 5%.

The used method of the temperature measurements is valid as long as conditions are invariant throughout the observed volume and until the particle absorption is predominated over the scattering. The former condition is fulfilled in the shock tube when the boundary effects or the deposition of particles on the windows with their further cooling-down process can be neglected. According to

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