Available online at www.sciencedirect.com
ScienceDirect
Proceedings of the Combustion Institute xxx (2014) xxx–xxx
Proceedings of the Combustion Institute
www.elsevier.com/locate/proci

Experimental study of soot size decrease with pyrolysis temperature rise

A. Emelianov [a], A. Eremin [a,*], E. Gurentsov [a], E. Mikheyeva [a,b], M. Yurischev [a]

[a] *Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia*
[b] *Bauman Moscow State Technical University, Moscow, Russia*

Abstract

Simultaneous measurements of the temperature dependencies of the size, growth rate and relative yield of soot particles were carried out in the shock wave pyrolysis of various carbon-bearing species (carbon suboxide –C_3O_2, acetylene –C_2H_2 and benzene –C_6H_6). In all substances studied in the temperature ranges from 1800–2000 K to 2500–3000 K, a sharp fall in soot size accompanied by a sharp increase in the rate of their formation was observed. Analysis of the data obtained showed that the decrease of soot particle size and decrease in total time of their formation with the temperature rise obey similar exponential dependencies, which could be qualitatively correlated with an increase in the rate of decomposition of the initial carbon bearing molecules. It is established that the observed decrease in the total time of soot particle growth with increased temperature is caused by a decrease in their final size, and the decrease of extinction at 633 nm reflects not a reduction of soot yield, but a decrease in the extinction coefficient upon the reduction of soot particle size. Extinction measurements on a shorter wavelength (220 nm and 248 nm) indicated an approximately constant soot yield in the specified temperature range.

Keywords: Soot size; Shock wave pyrolysis; Temperature dependence; Total time of soot formation; UV and visible extinction

1. Introduction

In combustion and pyrolysis of carbon bearing species, the size of soot particles formed at different temperatures does not remain invariable. In a number of works, a so-called bell-shaped temperature dependence of the soot particle size in shock wave pyrolysis conditions has been observed [1–4]. The shape of this dependence is very similar for various species and up to temperatures of about $T_{max} = 1600–2000$ K, the size of soot particles increases, while with further rises in temperature, it steadily decreases. The maximum particle size corresponds to the typical sizes of soot of 15–30 nm, and at temperature increases up to 2500–3000 K, it falls to 2–5 nm. There is neither a clear physical interpretation nor a model description of this phenomenon in the literature.

---

[*] Corresponding author. Address: Joint Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya 13, Moscow 125412, Russia. Fax: +7 (495) 495 79 90.

E-mail address: eremin@ihed.ras.ru (A. Eremin).

http://dx.doi.org/10.1016/j.proci.2014.08.030

Please cite this article in press as: A. Emelianov et al., *Proc. Combust. Inst.* (2014), http://dx.doi.org/10.1016/j.proci.2014.08.030

Note that in flames the particle size distribution function is also dependent on temperature. At $T < 1850$ K flames are characterized by the bimodal particle size distributions, which at higher temperatures transform to unimodal [5]. Similar transformation from small particles, called nano-organic carbon (NOC), to usual soot particles takes place at any flame temperatures with increasing of height above the burner (HAB) [6]. The mechanism of formation of second maximum on particle size distribution proposed in [5] is particle–particle coagulation, which is inhibited at high temperatures and apparently has no enough time at the small HAB.

However, the conditions in shock wave pyrolysis are very different from flames. The temperature range is much higher (2000–3000 K), while the time scale is very short – the total observation time is about 1 ms. In these conditions the particle–particle coagulation is negligible at any temperatures. Besides that, the decrease of particle size with the temperature rise in various hydrocarbons [1,2,4] and hydrogen free precursors [3] is absolutely similar. Therefore the reasons of particle size decrease at the temperatures $T > 2000$ K in shock wave pyrolysis conditions are evidently other from flames.

Importantly, the bell-shaped temperature dependence of the soot particle size observed in pyrolysis conditions is quite similar to the well-known temperature dependence of soot yield, usually presenting a bell-shaped curve with a maximum in the same temperature range (see review [7] and references within). The reason for the increase of the yield and the final soot size with increasing temperature on the left branch of a bell-shaped curve does not usually raise doubts – it is an increase in the degree of decomposition of the initial carbon bearing molecules. However, the reason for the decrease in soot yield at temperatures above T_{max} is not so obvious. These temperatures are much less than the characteristic temperatures of phase transitions in carbon (so all carbon has to be in condensed state), and at the same time, the stability of all gaseous carbon-bearing molecules inevitably decreases with the temperature growth. As it was shown in [5,8] the ability of survival and dimerization even for heaviest and most stable hydrocarbons of coronene group (like circumcoronene $C_{54}H_{18}$), exponentially decreases at the temperatures above 2000 K. Therefore the existence of any stable hydrocarbon molecules at the temperatures 2500–3000 K looks very improbable. One can add that the electron microscopic analysis of small particles (<10 nm) formed from hydrogen free precursors C_3O_2 and CCl_4 at these high temperatures has shown that they consist of pure carbon and have the same structure of amorphous graphite as usual soot particles (20–40 nm) [3,9]. Therefore the presence of small NOC particles (less than 10 nm in size) observed in flames [5,6] in high temperatures pyrolysis conditions is very unlikely. Thus one can assume that after the pyrolysis of any carbon bearing species at the temperatures 2500–3000 K only carbon particles of different size, which we would attribute to soot-like particles and simple stable gas molecules (like H_2, H, CO, Cl, etc.) remain in the mixture.

Note that the value of the soot yield is usually extracted from extinction measurements at wavelengths of 633 nm. In review [7], it was assumed that the apparent fall in soot yield is actually connected with the decrease in size of the formed particles, resulting in a decrease of their refractive index at this wavelength.

It is known that a decrease in the size of carbon particles leads to changes in the spectral distribution of their refractive index [10–12]. Donn [10] had shown that the spectral distribution of mass extinction coefficient of pure graphite spheres according to Mie theory is essentially changing when particle size is falling down. The particles of usual soot size 15–30 nm are practically grey; i.e. they intensively absorb radiation in all visible and near-IR spectral ranges, while upon a decrease in size to 5–10 nm, their range of extinction is shifted towards short wavelengths. Such particles become transparent for wavelengths of more than 400–500 nm, but still absorb well at $\lambda < 400$–300 nm. The broadening of extinction spectra from UV to visible and near IR range during the growth of hydrogen free carbon particles in shock wave pyrolysis of C_3O_2 was reported in [9]. Similar data of broadening of extinction spectra with time were presented for shock wave pyrolysis of toluene [13]. The direct observation of the sharp rise of extinction at $\lambda = 1.06\ \mu$ when soot particles grow more than 10 nm in size was reported for ethylene/air flames [11] and shock tube pyrolysis of acetylene [12]. The similarity of behaviour of extinction spectra for hydrogen free carbon particles [9] and small soot particles formed from various hydrocarbons [13,14] in shock wave pyrolysis conditions allows neglecting the possible input of heavy hydrocarbons in UV extinction, moreover the mass extinction coefficients of all hydrocarbons are less than those for small carbon nanoparticles [10]. Therefore we will regard all extinction observed in high temperature pyrolysis of various carbon bearing species to the soot particles of different size.

Another important characteristic of soot formation process is the total time of particle growth. Usually, researchers allocate three various stages of this process: the induction period, surface particle growth and coagulation. Shock tube experiments in most cases only allow observation of the first two stages of the process due to the restriction of working time, and these stages are significantly accelerated with temperature growth. A sharp decrease of induction time with the