



Temperature of Detonation of Hydrocarbon Measured with a Two-color Pyrometer

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Abstract

The temperature of detonations of mixture of acetylene and oxygen at various ratios were measured by using a two-color pyrometer we made in the lab. The pyrometer was calibrated with standard solar spectrum published by ASTM. The measured temperature increased with oxygen content in pre-detonation mixture in the reaction chamber and was as high as about 4000 K at higher oxygen content.

Keywords: Temperature; Oxygen; Hydrocarbon

Introduction

We have recently invented and patented the hydrocarbon detonation technique to mass produce graphene nano-sheets. For a typical detonation, the chamber is evacuated via the vacuum pump and it is filled up to one atmosphere pressure with hydrocarbon and oxygen in desired ratio. Electric spark is given into the chamber by tesla coil or spark generator ignition system connected to the power supply. The chamber is then cooled, and the carbon formed inside will be collected for characterization. Raman Spectroscopy, X-ray powder diffraction, and Transmission Electron Microscopy show that the carbon formed is pristine graphene. We hypothesize that the detonation built in situ temperature should be very high enough to graphitize detonation produced unburned carbon aerosols into graphene. We used a two-color pyrometer to measure the detonation temperature. A description of theory, calibration and performance of a two-color pyrometer that we made to measure detonation temperature is presented in this work.

Theory

The temperature of detonation of hydrocarbons, we hypothesize, is very high and hence the surface temperature of the detonation produced material is assumed to be higher than the

gold point (1064.43°C). A radiation thermometer or pyrometer is suitable to measure the surface temperatures above gold point [1]. A pyrometer is based on the Planck's law for black body radiation and it is given as

$$q_{b\lambda}(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

Where, $q_{b\lambda}(T)$ is spectral emissive power of the black body and it is function of wave length ' λ ' and temperature ' T ' of the body. ' k ' is Boltzmann constant. For simplicity, the following constants are redefined in the above equation.

$$C_1 = 2hc^2 \text{ and } C_2 = \frac{hc}{k}$$

Now the equation for Planck's law becomes,

$$q_{b\lambda}(T) = \frac{C_1}{\lambda^5} \frac{1}{e^{\frac{C_2}{\lambda T}} - 1} \text{------(1)}$$

Figure 1 shows a plot of λ versus q in equation (1) for $T=3000K$ and $5000K$. If we know the emissive power at any

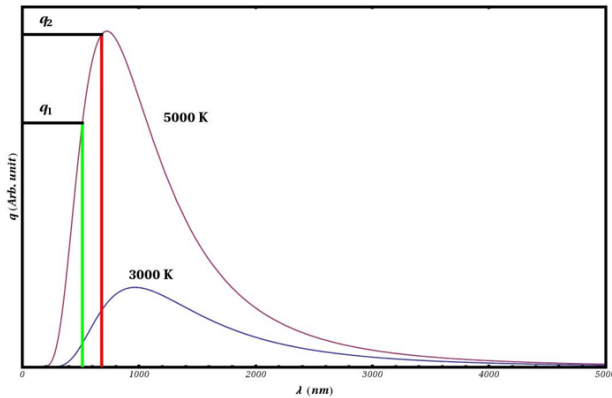


Figure 1: Planck's law of black body radiation for T= 3000K and 5000K.

known wavelength, say 515 nm (green) or 680 nm (red), of the radiation emanating from the hot surface, the temperature of the corresponding surface can be determined. This concept is used to make a pyrometer. The mathematical steps, based mainly on the reference [1], presented below show how the temperature of a hot surface will be derived by using this concept.

For small wavelengths, $\frac{C_2}{\lambda T} \gg 1$, so '-1' in the denominator of equation (1) can be dropped for simplicity.

$$q_{b\lambda}(T) = \frac{C_1}{\lambda^5} \frac{1}{e^{\frac{C_2}{\lambda T}}} \text{----- (2)}$$

This is called Wien's approximation to Planck's law and it is considered as the theory of pyrometer.

In addition to the simplicity in calculations, the errors, in the calculation of temperature, committed by using Wien's approximation is nominal [1]. For example, the maximum error that comes due to this approximation at 6000K is only about 1.3% for radiation of a wavelength of 550 nm as shown in figure 2.

For a design of the pyrometer, it is necessary to define brightness temperature, which is the temperature of true black body at which it has the same emissive power equal to that of actual body surface at a particular wavelength [1].

$$q_{a\lambda}(T_a) = q_{b\lambda}(T_b) \text{----- (3)}$$

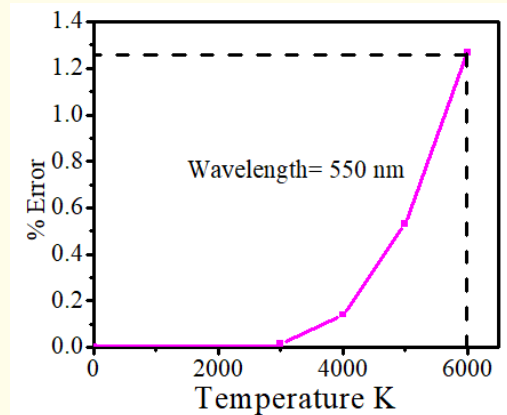


Figure 2: Error due to Wien's approximation.

Where T_a is the temperature of the actual surface and the T_b is the brightness temperature.

When the body is not a black body, like a burning carbon aerosol, the term emissivity, e_λ , which actually tells how close is the radiation from a body is to that from a true black body is used. $e_\lambda < 1$ for real object, and $e_\lambda = 1$ for a perfect black body. So, it is obvious that $T_a > T_b$ because of the emissivity of the actual surface.

From equations (2) and (3), we can write,

$$e_\lambda \frac{C_1}{\lambda^5} \exp\left(-\frac{C_2}{\lambda T_a}\right) = \frac{C_1}{\lambda^5} \exp\left(-\frac{C_2}{\lambda T_b}\right) \text{----- (4)}$$

This gives, $e_\lambda \exp\left(-\frac{C_2}{\lambda T_a}\right) = \exp\left(-\frac{C_2}{\lambda T_b}\right)$

$$e_\lambda = \exp\left[C_2/\lambda \left(-\frac{1}{T_b} + \frac{1}{T_a}\right)\right]$$

$$\frac{1}{T_a} - \frac{1}{T_b} = \frac{\lambda}{C_2} \ln(e_\lambda) \text{----- (5)}$$

This is ideal pyrometer equation.

The basis for a two-color pyrometer is that the ratio of emissive power of the actual surface at two very close wavelengths λ_1 and λ_2 should be same as the corresponding ratio for the black body. Moreover, the emissivity of the surface at the chosen wavelengths needs to be equal or very close to each other [1].

$$\frac{q_{a\lambda_1}(T_a)}{q_{a\lambda_2}(T_a)} = \frac{q_{b\lambda_1}(T_b)}{q_{b\lambda_2}(T_b)} \text{----- (6)}$$

From equations (2) and (6),

$$\frac{e_{\lambda_1}}{e_{\lambda_2}} \exp \left[\left(-\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right) \frac{C_2}{T_a} \right] = \exp \left[\left(-\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right) \frac{C_2}{T_b} \right]$$

$$\exp \left[\left(-\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right) C_2 \left(\frac{1}{T_a} - \frac{1}{T_b} \right) \right] = \frac{e_{\lambda_2}}{e_{\lambda_1}}$$

$$\frac{1}{T_a} = \frac{\ln \left(\frac{e_{\lambda_2}}{e_{\lambda_1}} \right)}{C_2 \left(-\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right)} + \frac{1}{T_b} \text{ ----- (7)}$$

In equation (7), the term $\frac{1}{T_b}$ in the right side can be eliminated as follows.

The emissive powers of black body at temperature T_b at wavelengths λ_1 and λ_2 are given by Wien’s approximation:

For λ_1 , $q_{b\lambda_1}(T_b) = \frac{C_1}{\lambda_1^5} \exp \left(-\frac{C_2}{\lambda_1 T_b} \right)$

For λ_2 , $q_{b\lambda_2}(T_b) = \frac{C_1}{\lambda_2^5} \exp \left(-\frac{C_2}{\lambda_2 T_b} \right)$

Now,

$$\frac{q_{b\lambda_1}(T_b)}{q_{b\lambda_2}(T_b)} = \left(\frac{\lambda_2}{\lambda_1} \right)^5 \exp \left[\frac{C_2}{T_b} \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \right] \text{ ----- (8)}$$

From the condition for two color (or ratio) pyrometer mentioned in equation (6), using equation (8),

$$\frac{q_{a\lambda_1}(T_a)}{q_{a\lambda_2}(T_a)} = \left(\frac{\lambda_2}{\lambda_1} \right)^5 \exp \left[\frac{C_2}{T_b} \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \right]$$

$$\frac{1}{T_b} = \frac{\ln \left[\frac{q_{a\lambda_1}(T_a)}{q_{a\lambda_2}(T_a)} \left(\frac{\lambda_1}{\lambda_2} \right)^5 \right]}{C_2 \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)} \text{ ----- (9)}$$

Substituting equation (9) in equation (7),

$$\frac{1}{T_a} = \frac{\ln \left(\frac{e_{\lambda_2}}{e_{\lambda_1}} \right) + \ln \left[\frac{q_{a\lambda_1}(T_a)}{q_{a\lambda_2}(T_a)} \left(\frac{\lambda_1}{\lambda_2} \right)^5 \right]}{C_2 \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)} + \frac{\ln \left[\frac{q_{a\lambda_1}(T_a)}{q_{a\lambda_2}(T_a)} \left(\frac{\lambda_1}{\lambda_2} \right)^5 \frac{e_{\lambda_2}}{e_{\lambda_1}} \right]}{C_2 \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)}$$

$$T_a = \frac{C_2 \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)}{\ln \left[\frac{q_{a\lambda_1}(T_a)}{q_{a\lambda_2}(T_a)} \left(\frac{\lambda_1}{\lambda_2} \right)^5 \frac{e_{\lambda_2}}{e_{\lambda_1}} \right]} \text{ ----- (10)}$$

This is the equation used as principle to build a two-color pyrometer in the detonation lab.

Design and working equation

Figure 3 shows the schematic of the detonation chamber with the two-color pyrometer (detector) and dynamic pressure sensor. The optical detector consists of two band- pass filters centered at wavelengths = 515 nm (Edmund Optics, item number : 65-638) in green color and = 680 nm (Edmund Optics, item number: 67-770) in red color in the figure. The detonation flash light emergent from the quartz window of the chamber passes through the reflective neutral density filter (ND filter; Optical Density= 3.0, provided by Edmund Optics, item number: 46-126) and falls on these band-pass filters. The green and red light emerged through these filters then incident on the corresponding photodiodes. The electronic signal, proportional to the power of incident light, from the photodiodes will be acquired by data acquisition system (Model: NI USB-6210, National Instrument) and displayed on the computer in volts.

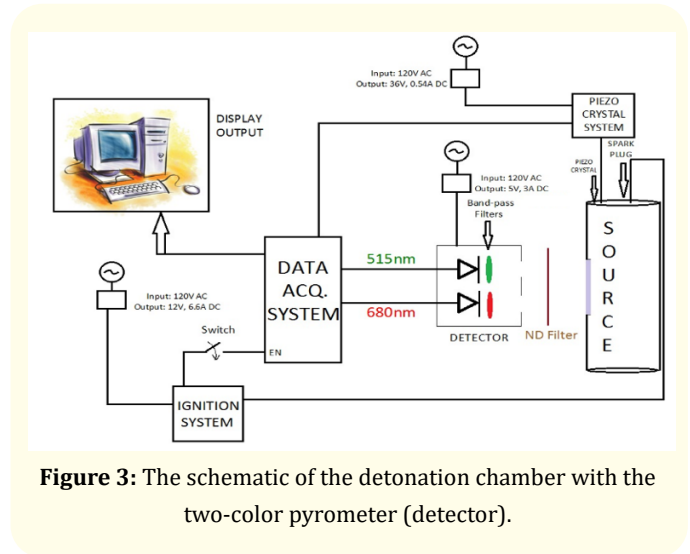


Figure 3: The schematic of the detonation chamber with the two-color pyrometer (detector).

The ratio of the peak value of the displayed signals in volts is basically the measured experimental ratio, R_{ex} , and it is equivalent to:

$$R_{ex} = \frac{\text{Power of signal of } \lambda_1}{\text{Power of signal of } \lambda_2} \text{ ----- (11)}$$

This value of will be compared with the assumed true ratio,

$$R_{true} = \frac{q_{a\lambda_1}(T_a)}{q_{a\lambda_2}(T_a)}$$

of emissive powers appeared in the denominator of equation (10) to get a calibration constant C from the relation,

$$R_{true} = C R_{ex}$$

Choosing the following numbers for constants,

$$C_2 = \frac{hc}{k} = \frac{6.6 \cdot 10^{-34} \text{ Js} \cdot 3 \cdot 10^8 \text{ m/s}}{1.38 \cdot 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}} = 0.0144 \text{ mK}$$

$$\lambda_1 = 5.15 \cdot 10^{-7} \text{ m}$$

$$\lambda_2 = 6.80 \cdot 10^{-7} \text{ m}$$

We get equation (10) as,

$$T_a = \frac{-6784.7}{\ln[C \cdot R_{ex} \cdot 0.2492]} \text{ --- (12)}$$

This is the working equation that is used to determine the temperature of a typical detonation in the lab.

Calibration and performance

A two-color pyrometer is usually calibrated by measuring radiation from a black body cavity furnace or melting tungsten filament. We did not use both of these standard calibrating tools and instead, we used an unconventional, cheapest and most abundant calibration tool- the sunlight. We have used the standard terrestrial solar radiation spectrum, figure 4, published by the American Society for Testing and Materials (ASTM) to calibrate the pyrometer we made. Legitimacy of this choice lies in the claim made by ASTM that the spectra are representative of average conditions in the 48 contiguous states of the United States of the places of a turbidity of 0.27 and a tilt of 37° facing the sun and a ground albedo of 0.2 [2]. Thus, the ratio of the emissive power at 515 nm to that at 680 nm from figure 4 was $R_{true} = 1.2$.

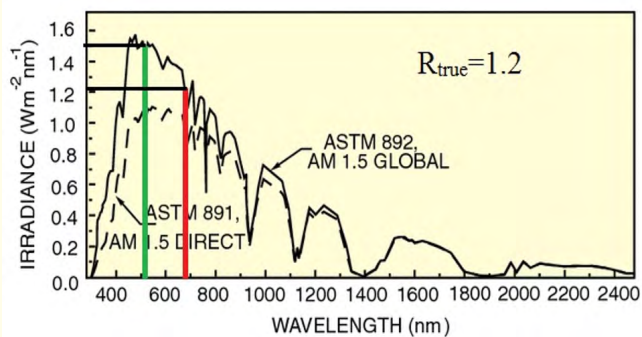


Figure 4: Standard spectra for AM 1.5. The direct spectrum is from ASTM E891 and global ASTM E892 [2].

The diffused sunlight was measured through the pyrometer we designed and got almost constant experimental ratio, $R_{ex} = 0.33$, in morning, afternoon and evening sunlight measured for about 4 weeks. Figure 5 shows the representative data.

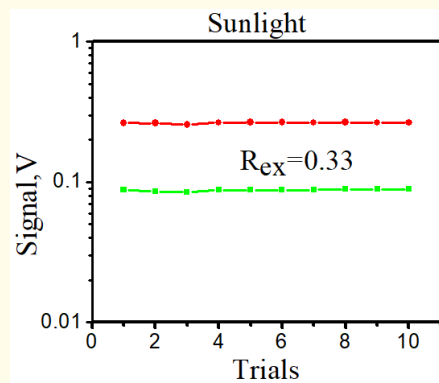


Figure 5: Measurement of sunlight with two-color pyrometer.

With $R_{true} = 1.2$ from figure 4 and $R_{ex} = 0.33$ from figure 5, the calculated calibration constant was found to be $C=3.6$ from $R_{true} = C R_{ex}$. As a test of this calibration tool, the temperature of the sun was determined by substituting C and R_{ex} in equation (12) and found to be $T_a = 5600 \text{ K} \pm 200 \text{ K}$. This is a very reasonable value for the temperature of sun’s surface and hence the choice of standard solar spectrum as a calibration tool seems okay. This calibrated two-color pyrometer was further tested by measuring the radiation of uniform intensity from three glowing tungsten filament lamps kept in series to determine the temperature of the source (tungsten filament giving off the light). The measured experimental ratio for lamp light was $R_{ex} = 0.13$ as shown in figure 6(a). The calibration constants calculated from this R_{ex} and four probable temperatures of filament lamps were plotted against the corresponding temperatures and kept along with the same graph for sunlight for comparison as shown in figure 6(b). The intersection point of the two lines is at $T_a = 3200 \text{ K} \pm 200 \text{ K}$ (figure 6 b) and it corresponds to the temperature of the tungsten filament lamp. This value of temperature is a reasonable value relative to that quoted value of temperature of a glowing filament of tungsten lamp.

The measured temperature of the sun and the filament lamp were precise enough to validate the choice of the standard solar spectrum as a calibration tool. The calibrated pyrometer was then used to measure the detonation temperatures. The signal intensity

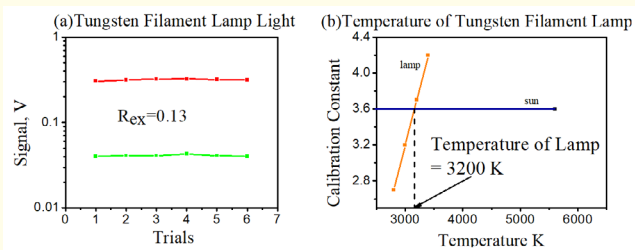


Figure 6: (a) Measurement of radiation from the filament lamp by the two color pyrometer and (b) determination of temperature of the lamp using the calibration constant from the measurement of sunlight.

detected by the pyrometer from light of wavelengths 515 nm and 680 nm coming off from a typical detonation and the corresponding peak detonation temperature calculated from equation (12) are shown in figure 7.

Figure 7 presents the signal of light intensity versus time after the ignition system is turned on acquired through pyrometer during the detonation which is completed in 40 ms. When the detonation flash light is higher than the background light, the intensity of the both signals recorded by pyrometer follow almost the same pattern of the variation with time and it continues for about 15 ms (see from 20 ms to 35 ms in figure 7). The peak detonation temperature corresponds to the temperature calculated where the intensity of the signals are maximum and it is around 3900 ± 200 K at 26 ms for the case shown in figure 7. In the detonation represented by figure 7, the maximum temperature appears to be ca. 4200K but does not occur at the maximum intensity. This discrepancy is due to the finite experimental error. Temperatures lower than ca. 2000K are supposed impossible be measured accurately with the present pyrometer design. Nevertheless, it is apparent that the rapid cooling from the peak temperature occurs in ca.6 ms [3].

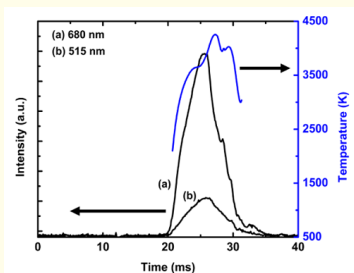


Figure 7: Signals of intensity of light versus time for a typical detonation acquired by the pyrometer system and the corresponding temperature after the ignition system is turned on [3].

As an additional independent cross-check of the correctness of the measured temperatures from the two-color pyrometer, the measured temperatures of detonations of mixture of acetylene (mole percentage from 50% to 95%) and oxygen were compared with those reported by the other groups earlier to this work. Figure 8 shows the temperatures of detonations determined by three different groups including us.

The measured temperature of detonation, qualitatively, increases from ca. 2700K (for 95% mole percentage of C_2H_2) to ca. 4300K (for 50% mole percentage of C_2H_2). These temperatures are almost consistent to the those measured by earlier groups as noticed in figure 8. So, we rely on the measurements of this pyrometer. Temperatures of all the detonations of hydrocarbon and oxygen mixture were determined by using this pyrometer.

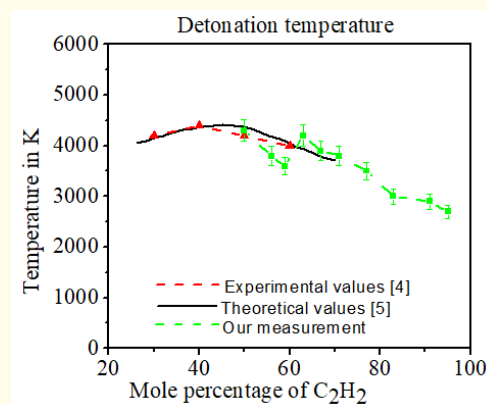


Figure 8: Comparison of temperature of detonation of acetylene and oxygen mixture measured by the two-color pyrometer with that determined by earlier works [4,5].

Conclusion

An unconventional calibration tool, standard solar spectrum, was used to calibrate a “home made” two color pyrometer to measure the hydrocarbon detonation temperatures. The measured detonation temperatures are as high as about 4000 K and this high detonation temperature could be the one of important factors to graphitize detonation carbon to graphene.

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