Smoke generation in black powder combustion

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It is well known that very large amount of smokes is produced in the black powder combustion. Smokes generated by explosive combustion of black powder often prevent visibility of the beautiful aerial fireworks displays in calm environment. Final goal of the present study is to understand the kinetic mechanism of fine particle formation in black powder combustion and to control the size and rate of particles so that aerial display fireworks can clearly be seen even in calm environment.

In general, the size of particles in smoke is ranging from several nm to 1 μm. White smoke can be observed with flame in black powder combustion. These white smokes are thought to be composed of nano-particles of K_2S, K_2CO_3 and K_2SO_4. At the best of our knowledge, no study has been performed in the past on the detailed chemical and physical mechanism for the very fast production of these very fine (order of nm size) smoke particles in black powder combustion.

Heterogeneous combustion process of black powder is extremely complex and many assumptions are required to model this process. Black powder is composed of potassium nitrate (KNO_3), charcoal (C), and sulfur (S). The products of black powder combustion differ according to its composition. The stoichiometry of a typical black powder can be represented by the following equation [1]:

$$4KNO_3(s) + 7C(s) + S(s) \rightarrow 3CO_2 + 3CO + 2N_2 + K_2CO_3(s) + K_2S(s). \quad (1)$$

Here, (s) represents that the species is in solid state. Solid state products of $K_2CO_3(s)$, $K_2S(s)$, and $K_2SO_4(s)$ can be the source of particulates produced by black powder combustion. Actual processes for particulates production can be extremely complex. Multi-phase chemical reactions and many physical and chemical processes such as vaporization, sublimation, and coagulation are involved. Typical black powder composed of KNO_3/C/S=75/15/10 wt% gives main gas phase products of CO_2, CO, N_2 and liquid phase products of $K_2CO_3(l)$, $K_2S(l)$, and $K_2SO_4(l)$, based on the equilibrium calculation. These liquid products will give solid residuals after products are cooled down by mixing with ambient air. These combustion products in condensed phase can be the source of particulate matter. A schematic of particle formation in black powder combustion is depicted in Fig. 1. Ignition of black powder starts with melting of ingredients [1].

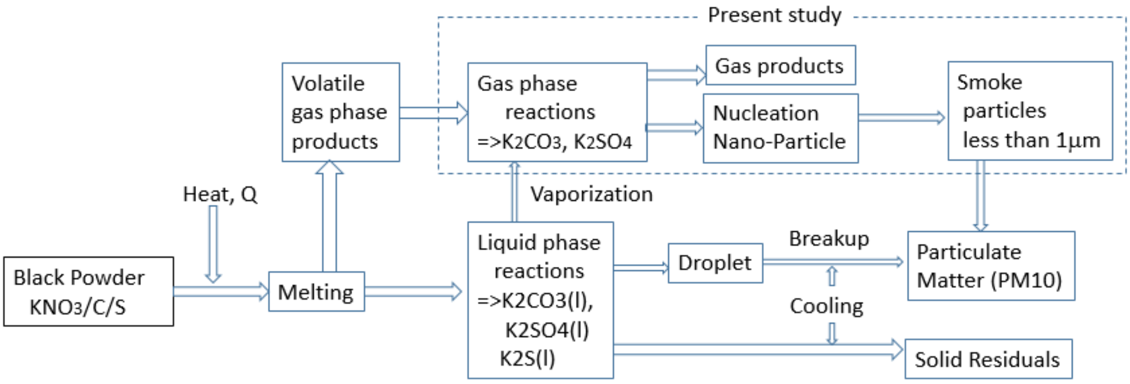

Figure 1 - Schematic diagram for particle formation in black powder combustion.

Exothermic reactions in liquid will produce K_2CO_3(l), K_2S(l) and K_2SO_4(l). Some prat of these liquid may form droplet and these droplets will breakup into smaller droplets. However it is impossible to form very fine particle (nano-particle) by these breakup processes. Too many breakup steps are required to reach nanometer size particles. Melting liquid also emits volatile gas phase molecules and gas phase reactions will produce K_2CO_3 and K_2SO_4 molecules. It is noted that color of smoke generated by black powder combustion is white and it is believed that smoke is composed of particles of K_2CO_3 and K_2SO_4.

In the present study, a new model to predict smoke formation in black powder combustion has been developed. The model includes two steps. At first, gas phase precursor molecules for nucleation are identified by performing partial equilibrium calculations, in which all products in condensed phase are excluded. Partial pressures of precursor molecules are also obtained by this calculation. Second, classical nucleation theory [2,3] is applied to predict critical radius and nucleation rate. The model is applied to predict smoke formation in black powder combustion. K_2CO_3 and K_2SO_4 are identified as precursor molecules. Thermodynamic properties of these precursors (vapor pressure, density in condensed phase, and surface tension) are estimated on the basis of literature data. Critical radius, $r*$, and rate of nucleation, J, for black powder combustion are estimated based on this model. Typical results are shown in Fig.2. Very small value of $r*$ is just the indication of very rapid rate of nucleation, as shown in the right panel in Fig.2. On the other hand, $r*$ value rapidly increases at $Y(S)$>17 wt% ($Y(X)$ is the mass fraction of component X) and corresponding nucleation rate, J, decreases sharply. This predicts that smoke particle composed of K_2CO_3 could not be produced with higher content of sulfur than 17 wt%. On the other hand, nucleation of K_2SO_4 shows opposite trend to

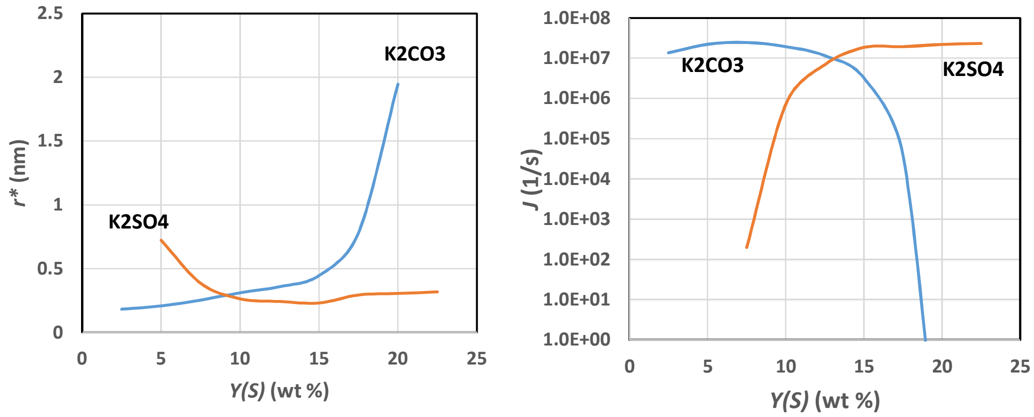

Figure 2 - Critical radius and rate of nucleation, *J*, for K_2CO_3 and K_2SO_4 in black powder combustion at constant pressure (p=1bar) and adiabatic condition as a function of mass fraction of sulfur, *Y(S)*. Mass fraction of KNO_3 is fixed to $Y(KNO_3)$=75 wt%.

K_2CO_3. Critical radius is almost constant at *Y(S)*>10 wt%, and increases gradually. It is expected that smoke particle composed of K_2SO_4 could not be produced with lower content of sulfur than 12 wt%. These results indicate that the standard black powder with 75 wt% of KNO_3 produces smoke particles very quickly. (Time constant of nucleation is less than 1 μs.) Compositions of smoke particle depend on mass fraction of sulfur. K_2CO_3 is the main component of smoke at sulfur lean ingredient and K_2SO_4 is the main at sulfur rich ingredient. Present model prediction seems to be consistent with our experience. Indeed, combustion of standard black powder generate large amount of white smoke with flame.

(References)

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