



Auto-ignition temperature and burning rate of potassium pool fire in a confined enclosure



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ABSTRACT

Due to their high reactivity, alkali metals pose a fire hazard as spontaneous ignition in air is possible in several high temperature applications. In the present study, the ignition and burning rates of a hot, shallow potassium pool of 0.06 and 0.10 m diameter have been studied experimentally. Thermodynamic equilibrium calculations of K–air system show that vapour phase combustion of potassium is possible. This has been verified experimentally. Over much of the duration of fire, the pool temperature is found to be in the 900–1000 K range; therefore, the oxides formed as a result of combustion would be molten and solid residues are formed only at the end of the fire, unlike in the case of sodium and lithium. Burning rate of potassium has been found to be in the range of 30–60 kg/m²s for various conditions and is typically lower than that of sodium and lithium under similar conditions. Auto-ignition temperatures lie in the range of 500–650 K, the higher temperatures occurring in smaller pools and low oxygen concentrations. Using different mass transfer scenarios, it is shown experimentally that the burning rate of potassium pool is limited by mass of transfer of oxidant.

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1. Introduction

Potassium is one of the members of alkali metals along with lithium, sodium, rubidium and cesium. Alkali metals are good reducing agents because of their strong tendency to attain inert gas electronic configuration. As rubidium and cesium are too reactive for safe handling, potassium is the most electropositive reducing agent used in the industry [1,2]. Potassium metal in molten form is atomised in air for producing potassium superoxide [3], which is used as an oxygen source in self-contained breathing apparatus. It is also used in the manufacture of potassium bases, potassium graphite (where it is used in molten state at 120–150 °C) and potassium hydride (at a temperature of about 200 °C). The indirect use of potassium is in the form of Na–K alloys. These Na–K alloys have excellent thermal and electrical conductivities which render them ideal for use as heat exchange fluids, cooling liquids in hollow valve stems, contact liquids for high temperature thermostats and homopolar generators, hydraulic fluids and stored chemical energy propulsion systems [1,2,4,5]. Another major application of alkali metals, especially lithium, sodium and potassium and their

alloys, has been in advanced nuclear power reactors such as fast breeder reactors (sodium and potassium) and lithium (fusion reactors). Fire and explosion hazards associated with sodium and potassium compounds in the fertiliser industry [6] and biodiesel production [7] has also been receiving attention lately.

Due to their high reactivity, alkali metals pose a fire hazard as spontaneous ignition in air is possible in several high temperature applications. Metal combustion has been studied extensively by many authors over the years owing to their potential use as additives to solid propellants in rocket motors. In this context, several metals such as beryllium (Be), boron (B), carbon (C), magnesium (Mg), aluminium (Al), silicon (Si), calcium (Ca), titanium (Ti), iron (Fe), copper (Cu), zinc (Zn), strontium (Sr), zirconium (Zr), molybdenum (Mo), barium (Ba), tantalum (Ta) and tungsten (W) have been studied by many research groups around the world. Several papers have appeared on fundamental aspects of metal combustion such as the ignition behaviour, flame temperature, burning rate, reaction mechanism with oxygen and thermodynamics of the condensed products. Recent reviews of the state of the art have been given by [4] and [8]. Alkali metal combustion is distinct from metal particle combustion due to the fact that alkali metals have relatively very low melting points when compared to other metals. Because of this, a variety of experimental configurations, namely, droplet combustion, liquid pool combustion and spray combustion configurations, have been used to study alkali metal combustion. The combustion products may include multiple stable oxides,

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peroxide with pure oxygen, hydroxide if moisture is present, and hydrides, nitrides, carbonates and bicarbonates, if suitable environment is provided. This aspect is unique to alkali metals when compared with other metals. Also, the condensed products are highly reactive as well as hygroscopic in nature which further makes their study complicated. An interesting observation related to alkali metal combustion is the formation of coral structured oxides [9–11].

Since alkali metals are vulnerable to highly exothermic reactions on exposure to both air and water, it is important to study the burning behaviour from the safety perspective. There is abundant literature on lithium [9] and sodium [10]. Ignition temperatures of lithium were studied in different atmospheres by several researchers [12–15]. Burning rates of lithium were reported in dry and moist air conditions for a range of initial mass quantities [16,17]. Products formed in aerosol and pan for lithium combustion were also studied [16,18,19]. Two kinds of sodium fire scenarios have been investigated, namely, spray fires and pool fires. Droplet combustion studies have also been conducted. Ignition temperatures have been reported for sodium pool fires [10,20–22], sodium spray fires [21,23,24] and sodium droplet combustion [21,25–27]. Burning rates of sodium were reported by several researchers in different environments [10,20–22]. Suppression and extinguishment of alkali metal pool fires has extensively studied or reviewed by many researchers [9,21,28] with specific focus on sodium and lithium.

There is comparatively little literature on potassium. Ignition temperatures of potassium in small cubical boxes ($5 \times 5 \times 5 \text{ mm}^3$ and $30 \times 30 \times 30 \text{ mm}^3$) were determined by Polykhalov and Prisyakov [29]. Optical constants of liquid potassium and radiation heat transfer between the planes bounding liquid potassium were studied by Kamiuto [30]. Ignition temperatures and fire extinguishment were studied for potassium along with other alkali metals by Rodgers and Everson [31]. Incipient bubble growth and transient pressure recovery for potassium during boiling were studied by Urata et al. [32]. A limited number of potassium pool fire data, in the context of alkali metal combustion, have been reported by Subramani and Jayanti [11]. Important information relevant to safety in handling potassium is not available. This provides the motivation for the present work which has the objective of determining the ignition temperature and burning rate of potassium pools in a confined enclosure which will be of specific interest to fire safety practitioners. To this end, experiments of potassium pool fire have been conducted in a $0.7 \times 0.7 \times 0.7 \text{ m}^3$ enclosure in which the effects of air flow pattern and the availability of oxygen on the ignition and burning rates have been studied. Details of the studies and the results obtained are discussed below.

2. Theoretical considerations in potassium pool fire

2.1. Criterion for vapour phase combustion

According to Glassman [4], a metal will burn in vapour phase combustion only if the volatilisation temperature of the metal oxide is greater than the boiling point of the metal. If the metal is more volatile than its oxide, the flame temperature will reach a level where the metal vapour pressure at that temperature moves the reaction zone off the metal surface. This form of combustion is shown by metals such as aluminium and magnesium [4,10]. Metals such as boron, molybdenum and tungsten undergo surface reaction. In the case of sodium and potassium, the melting point is low ($< 100^\circ\text{C}$) and a liquid pool or drop is formed before significant reactions take place. As the temperature is increased, a surface oxidation reaction occurs and the pool surface is usually covered by a porous layer of metal oxides. Vapour phase combustion can occur under distinct conditions [11]: (i) when the pool temperature is

sufficiently high that metal vapours penetrate through the porous oxide to form a vapour layer on the surface which then reacts with ambient air in a gas-phase reaction; and (ii) when the oxide layer melts or vapourises at high pool temperatures to present a clear pool of molten metal which can then participate in a vapour-phase combustion. An understanding of the metal–oxygen (air) thermodynamics is therefore essential. This is explored below.

2.2. Limiting temperature

Theoretical simulations considered in this present work have been carried out using NASA-CEA2 [33]. Chemical equilibrium is usually described by either of two equivalent formulations—equilibrium constants or minimisation of free energy. By employing the latter method, each species can be treated independently without specifying a set of reactions a priori, as required with equilibrium constants. Owing to this advantage, NASA-CEA2 code employs the latter method for estimating the equilibrium product compositions and adiabatic flame temperature for assigned thermodynamic states. These states may be specified by assigning two thermodynamic state functions such as temperature and pressure (t - p problem; used for construction of Mollier diagrams), enthalpy and pressure (h - p problem; used for combustion properties at constant pressure) and internal energy and volume (u - v problem; used for combustion properties at constant volume) [33]. In the present study, equilibrium calculations have been carried out as an h - p problem with initial temperature and pressure of 298 K and 1 atm, respectively. The equilibrium calculations were carried out by specifying the equivalence ratio, fuel as a K (cr) and oxidiser as O_2 . Validation of the calculations is in the form of comparison of the dominant composition of the pan or aerosol product. Experiments have been conducted by several researchers [2,18,19,34] to determine alkali metal combustion end products in both pan and aerosols. The NASA-CEA2 simulations carried out for Li, Na and K in three different equivalence ratios, namely, $\varphi < 1$, $\varphi = 1$ and $\varphi > 1$ —which would correspond to the conditions of formation of products in the aerosols, in the reaction zone and in the pan residue, respectively—predict the composition of the product. The predictions and reported data are compared in Table 1 below which shows good agreement. In addition, Subramani and Jayanti [11] compared the calculated adiabatic flame temperatures and measured peak flame temperature for lithium, sodium and potassium. These showed consistent variation.

In the present work, the procedure outlined by Glassman [4], and used earlier by the present authors for sodium–air system [35], has been followed to determine the volatilisation or limiting temperature of K- O_2 (at an equivalence ratio of 1) system. In these calculations heat is either added or removed from the system. An assigned enthalpy of zero corresponds to a standard ambient condition of 298 K temperature and 1 atm pressure. The decomposition characteristics at STP and stoichiometric conditions can be determined by adding or subtracting in the following way. The composition of the condensed phase changes during the transition over which the temperature remains constant. The enthalpy range over which the temperature remains constant is a measure of enthalpy of decomposition. (For a pure component, this would correspond to the latent heat of vapourisation.) This transition temperature is therefore called pseudo-boiling point [4,36]. It can be observed from Fig. 1 that for K- O_2 system, the major product formed at initial state is 0.353 mol fraction of K_2O (L). As the enthalpy is increased, K_2O (L) decreases and the decomposition of K_2O occurs at a constant temperature of 1825.7 K leading to the release of gaseous phase products K, K_2O , KO and O_2 . When the assigned enthalpy reaches 1.95 kJ/g of reactants, condensed K_2O is completely dissociated. When the enthalpy is withdrawn from the system, again temperature remains constant but condensed K_2O

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