Research Paper

Active substances study in fire extinguishing by water mist with potassium salt additives based on thermoanalysis and thermodynamics

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HIGHLIGHTS

- The MECs of six potassium salts were tested to enriched the database of water mist.
- The active substances are creatively obtained by thermoanalysis experimental method.
- The quantitative analysis is obtained through thermodynamics method.
- Extinguishing occurred by water, K cations, flame radical, and other anions.

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ABSTRACT

The active substances during the process of fire extinguishing by water mist with potassium salt additives was studied. The minimum extinguishing concentration (MEC) experiment results showed that K$_2$CO$_3$ have the most benefit in improving the fire extinguishing efficiency of pure water with the improving rate of 37.6%, 47.2% and 64.8% which the mass percent was 1%, 2% and 5%, respectively. Other potassium salt additives followed the order by: K$_2$C$_2$O$_4$ > CH$_3$COOK > KNO$_3$ > KCl > KH$_2$PO$_4$, and the reason attributed to the different active substances decomposed from flame temperature by different kinds of potassium salt additives. Thermoanalysis and characterization of the pyrolysis products of potassium salt solutions at flame temperature were analyzed through TG-DSC, XRD, and SEM, the results showed the KOH was the main product in the high extinguishing performance of potassium salts in flame chemical reactions. Thermodynamics analysis by HSC CHEMISTRY showed the K$_2$CO$_3$ could provide 4.85% KOH in equilibrium substances, which well above other potassium salts, and other active substances good for fire extinguishing benefited from the intermediate product during the process of the KOH reacted with the flame free radicals.

1. Introduction

In recent years, as the rapid development of the economic development, energy has become an important guarantee for the development of energy issues and even directly restricts the economic development. With the increase of population density and building, as well as the increased fuel consumption, fuel structure has been changed, gaseous fuel such as coal gas, liquefied petroleum gas and natural gas gradually becomes the main fuel for city life [1].

However, the widespread use of natural gas increasing the risk of natural gas leakage and fire and explosion accidents. CH$_4$ fire threatening the life security of the public and causing great damage to the material property. How to solve the CH$_4$ fire better become the research focus of fire science. Water is a main method for the treatment of fire since ancient times. With the continuous development of society, the fire form is constantly updated, and with the progress of science and technology, the form of water is also constantly innovating. The method of using water to treat fire has been greatly improved, and the water mist is the most representative of fire treatment means [2].

The addition of additives in fine water mist can enhance the fire extinguishing efficiency of pure water according to various studies on the fire extinguishing efficiency of additives [3–9]. In these researches, the water mist additives include KCl, NaCl, CH$_3$COOK, LiI, NiCl$_2$, CoCl$_2$, NaHCO$_3$, NaOH, CaCl$_2$, MgCl$_2$, FeCl$_3$, and MnCl$_2$. Experiments showed that the additives with the highest efficiency are the compounds of Fe and K [10]. Toxicity and cost problems resulted in the limited application of the Fe compound as an additive [11], which made potassium salts the focus of the present research.
The potassium salts decomposed at the flame temperature, and the fire extinguishing occurred with the reaction between the generated substances and flame radical by the chain termination reaction. The detailed methane pyrolysis process was GRI3.0, which contained 53 species and 325 reactions [12]. Warnatz [13] proposed that due to the slow chemical reaction rate of N in the CH₄ oxidation process, some C species has been rapid oxidation of COₓ before reactive with some N species. Therefore, the production of some N containing species is much smaller in the whole reaction process, which most detailed chemical reaction mechanism containing N species could negligible, while OH, H, O, CH, CH₂ were mainly components during methane pyrolysis. Venkata [14] also confirmed COₓ and H were the main species in methane decomposition. Based on a premixed flame burner, Mitani [15] proved that alkali metal salt additives can induce chemical extinguishment by eliminating free radical came from CH₄ pyrolysis through gas-phase homogeneous reaction. Zhang [16] reported that gaseous KOH could inhibit OH and H free radical in methane pyrolysis, generated intermediate transition KO and K, which combined with OH or H to generate gaseous KOH again. The content of the free radicals in the flame propagation process was decreased by catalytic reaction and indeed inhibited the pyrolysis reaction.

Previous studies on active substances in fire extinguishing by potassium salts mainly through the change of OH radical concentration in flame doped with K element, fit the chemical reaction rate function and inferred possible mechanisms by designing different burner. Firedman [17] studied the extinguishing effect of K stream through a clashing flame experiment and demonstrated that KOH is the extinguishing active substance in potassium salts by combining the equilibrium products and possible reaction pathways. Based on the chemical equilibrium computation with the updated database, Machale [18] further confirmed that the active product in the extinguishing reaction of potassium salts is gaseous KOH. However, due to the difficulty in measuring the concentration of OH radical in the experiment, the accuracy and repeatability was uncertain. Furthermore, for lack of uniform experimental design, the results obtained from different researchers are quite different. For example, the flame reaction doped with potassium salts, Slack [19] reported the fitting results of the rate constants for the critical reactions K + OH + M = KOH + M was 5 × 10⁻³² cm⁶/molec² s⁻¹ (T = 2000 K), while Patrick and Golden [20] calculated the same rate constants was 1.9 × 10⁻²⁵ cm⁶/molec² s⁻¹ (T = 2000 K); Husain [21] got the fitting results of the rate constants expression for the reaction K + O₂ + M = KO₂ + M was 1.89 × 10⁻²² T⁻²·⁶⁸, while Silver [22] gave the fitting result was 1.19 × 10⁻¹⁰ T⁻⁰·₃₆. These studies showed that the extinguishing active substance of potassium salts may theoretically be KOH, which has not been verified by a compelling experiment yet.

In the present study, six common potassium salts K₂C₂O₄, CH₃COOK, K₂CO₃, KNO₃, KCl, and KH₂PO₄ were chosen, a reliable and repeatable experimental method based on classic thermoanalysis in proving active substances during extinguishing process by water mist with potassium salt additives was reported. In addition, the minimum extinguishing concentration (MEC) of these potassium salts were tested by an improved cup burner was also investigated. Furthermore, the relationship between the extinguishing efficiency and the amount of active substances was proposed through thermodynamics by HSC CHEMISTRY6.

2. Experimental equipment and method

2.1. Cup-burner experiment

Fig. 1 shows the cup burner device. The experiment method is the same as Ref. [7].

2.2. TG-DSC experiment

Thermoanalysis of chemical extinguishing substances was used to measure the dependence of the characteristic parameters of the substances on temperature. Thermoanalysis can provide thermodynamic parameters and chemical reaction kinetic parameters of materials. At present, the most common method of studying thermostability of substances include differential scanning calorimetry (DSC), thermogravimetry (TGA), and differential thermal analysis (DTA). A chemical extinguishing agent only decomposes into extinguishing active substances under burnt temperature and thereby develops its chemical extinguishment capacity after the active substances have already reacted with flame radicals. Thermoanalysis has been highly appreciated by Chinese and foreign scholars in studying the decomposition mechanism of chemical extinguishing substances and possible extinguishing active substances.

TGA and DTA of six potassium salts in atmosphere were implemented by TGA-DSC synchronous tester of Switzerland METTELER Company. The reference compound was α-Al₂O₃, and the air inflow rate was 50.0 mL min⁻¹.

2.3. XRD and SEM experiment

The cup burner test system was improved to collect the pyrolysis products of water mist after ultrasonic atomization under
different heating temperatures. The chimney unit was replaced by a tube type resistance furnace for electric heating. The highest heating temperature, total heating power, and temperature control accuracy were 1100 °C, 20 kW, and ±1 °C, respectively. TEX-C100 temperature controller was used. The tube type resistance furnace has one reaction tube, in which fogdrop gained from ultrasonic atomization can directly induce conversion reaction. This reaction tube was made of materials with high temperature resistance, corrosion resistance, good heat transmission, and temperature change tolerance. An axial flow fan and a product collection bottle were set at the top of the tube type resistance furnace. Collected target powder was analyzed by D8-Advance X-ray diffractometer, and its surface microstructure was observed by the S4700 cold field emission SEM.

3. Results and discussion

3.1. MEC of potassium salt solutions

Theoretically, the MEC of water mist containing potassium salts is a fixed value. However, in this experiment, the concentration of water mist containing additives was adjusted by changing the working voltage of the atomization modules and their number. Therefore, concentration changed discontinuously, and the upper and lower limits of the MEC were observed. Extinguishing concentration using the upper and lower limits may extinguish fires successfully or unsuccessfully. Test results of MEC of six potassium salt solutions are listed in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Agent</th>
<th>Upper limit of MEC</th>
<th>Lower limit of MEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>12.11</td>
<td>10.07</td>
</tr>
<tr>
<td>1% K₂CO₃</td>
<td>7.56</td>
<td>6.98</td>
</tr>
<tr>
<td>2% K₂CO₃</td>
<td>6.39</td>
<td>5.08</td>
</tr>
<tr>
<td>5% K₂CO₃</td>
<td>4.26</td>
<td>3.95</td>
</tr>
<tr>
<td>1% K₂C₂O₄</td>
<td>8.38</td>
<td>7.78</td>
</tr>
<tr>
<td>2% K₂C₂O₄</td>
<td>7.96</td>
<td>7.25</td>
</tr>
<tr>
<td>5% K₂C₂O₄</td>
<td>4.51</td>
<td>3.75</td>
</tr>
<tr>
<td>1% CH₃COOK</td>
<td>8.85</td>
<td>6.76</td>
</tr>
<tr>
<td>2% CH₃COOK</td>
<td>6.05</td>
<td>5.75</td>
</tr>
<tr>
<td>5% CH₃COOK</td>
<td>5.04</td>
<td>4.63</td>
</tr>
<tr>
<td>1% KNO₃</td>
<td>10.8</td>
<td>8.6</td>
</tr>
<tr>
<td>2% KNO₃</td>
<td>8.34</td>
<td>6.71</td>
</tr>
<tr>
<td>5% KNO₃</td>
<td>5.05</td>
<td>3.43</td>
</tr>
<tr>
<td>1% KCl</td>
<td>9.34</td>
<td>7.13</td>
</tr>
<tr>
<td>2% KCl</td>
<td>7.95</td>
<td>6.84</td>
</tr>
<tr>
<td>5% KCl</td>
<td>6.97</td>
<td>4.62</td>
</tr>
<tr>
<td>1% KH₂PO₄</td>
<td>9.16</td>
<td>7.68</td>
</tr>
<tr>
<td>2% KH₂PO₄</td>
<td>10.12</td>
<td>8.48</td>
</tr>
<tr>
<td>5% KH₂PO₄</td>
<td>10.63</td>
<td>8.91</td>
</tr>
</tbody>
</table>

3.2. Thermal analysis of potassium salts

TG-DSC results of the six potassium salts at a temperature rate of 10 °C min⁻¹ are shown in supplementary materials and the results are shown in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Potassium salts</th>
<th>Temperature range (°C)</th>
<th>Thermal decomposition procedure</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃</td>
<td>62.54–125.27</td>
<td>K₂CO₃ + 2H₂O K₂CO₃ + 2H₂O</td>
<td>20.69</td>
</tr>
<tr>
<td>K₂C₂O₄</td>
<td>84.13–110.32</td>
<td>K₂C₂O₄ + H₂O K₂C₂O₄ + H₂O</td>
<td>21.15</td>
</tr>
<tr>
<td>CH₃COOK</td>
<td>313.07–606.85</td>
<td>2CH₃COOK → K₂C₂O₄ + C₂H₆</td>
<td>9.783</td>
</tr>
<tr>
<td>KNO₃</td>
<td>602.44–740.82</td>
<td>2KNO₃ → 2K₂O + O₂</td>
<td>10.68</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>207.98–271.01</td>
<td>2KH₂PO₄ → K₂H₂PO₄ + H₂O</td>
<td>16.87</td>
</tr>
<tr>
<td></td>
<td>291.76–358.78</td>
<td>K₂H₂PO₄ → 2KPO₃ + H₂O</td>
<td>15.31</td>
</tr>
</tbody>
</table>

In conclusion, potassium salt additives can improve the fire extinguishing efficiency of water mist. The degree of improvement in the fire extinguishing efficiency of the said additives is ranked as follows: K₂CO₃ > K₂C₂O₄ > CH₃COOK > KNO₃ > KCl > KH₂PO₄. Additives influence fire extinguishing efficiency mainly by increasing chemical actions and reducing the competition between the evaporative capacities of pure water. The fire extinguishing efficiency of K₂CO₃, K₂C₂O₄, CH₃COOK, KNO₃, and KCl solutions increased with increasing concentration. This effect indicates that the degree of increase in chemical actions is greater than the weakening of the evaporative capacity of pure water. The fire extinguishing efficiency of KH₂PO₄ solution decreased with increasing concentration. Hence, the chemical fire extinguishing capacity of the two salts is weak. Increasing concentration dominates the competitive relation for reducing the evaporative capacity of pure water.
corresponding the temperature range of 565.04–689.84 °C, with weightlessness rate of 15.02%. The results quite agreement with the present study testified the decomposition process of K₂C₂O₄, and the experimental error is within the allowable range.

DSC curve for CH₃COOK shows the endothermic peak and two exothermic peaks. The corresponding TG curve has two weight loss platforms. The endothermic peak is within 285.16–316.74 °C, and the peak temperature is 303.56 °C. The TG curve reveals that no weight loss occurred during this process. According to the test results of the X-4 microscopic melting point apparatus, the peak temperature is the melting point of CH₃COOK. The TG curve reflects CH₃COOK decomposed within the range of 313.07–606.85 °C with two corresponding exothermic peaks on the DSC curve, which shows that the thermal decomposition of CH₃COOK is completed in two steps. The first exothermic peak temperature is 416.77 °C, with the weight loss rate of 13.78%, and the exothermic enthalpy is 1220.60 J g⁻¹. The second exothermic peak temperature is 488.68 °C, with the weight loss rate of 13.01%, and the exothermic enthalpy is 926.52 J g⁻¹. Fleming [27] showed that the aqueous of CH₃COOH had better performance of extinguishing than pure water illustrated the CH₂COOH could decomposed in flame temperature and demonstrated the results of Huttinger.

DSC curve for KNO₃ shows the three endothermic peaks and the corresponding TG curve has one weight loss platform. The first endothermic peak is within 128.47–150.16 °C, and the peak temperature is 130.92 °C. The TG curve reveals that no weight loss occurred in this process. According to the test results of the X-4 microscopic melting point apparatus, the peak temperature is not the melting temperature but may be the endothermic peak caused by crystal transfer of KNO₃. The second endothermic peak is within 300.14–342.16 °C, and the peak temperature is 326.5 °C. According to the test results of the X-4 microscopic melting point apparatus, the peak temperature is not the melting temperature but may be the endothermic peak caused by crystal transfer of KNO₃. The second endothermic peak is within 300.14–342.16 °C, and the peak temperature is 326.5 °C. According to the test results of the X-4 microscopic melting point apparatus, the peak temperature is 326.5 °C. The TG curve reflects the decomposition process of KNO₃ within the range of 602.44–740.82 °C with one corresponding endothermic peak on the DSC curve, a peak temperature of 681.46 °C, and weight loss rate of 66.72%. The reaction absorbs a lot of heat when the endothermic enthalpy is 1867.55 J g⁻¹. Zhang [28] described the decomposition process of KNO₃ in oil flame environment and pointed out that K₂O, which generated from the decomposition reaction was the main substance in fire suppressing. While the experiment results of Wang [29] showed that the decomposition process of KNO₃ would be activate in the presence of C condition, which demonstrated the decomposition process and products.

DSC curve for KCl shows that the endothermic peak is within 758.61–779.18 °C, and the peak temperature is 769.62 °C, indicating that the endothermic peak is the melting point based on the melting point of KCl (771 °C) [23]. The TG curve indicates that KCl is very stable, and almost no weight loss occurred before the melting point. When the KCl reached the melting point, due to the high saturated vapor pressure of KCl, a part of the KCl volatile gas was blown off from the crucible as driven by the purge gas, which led to the loss of weight. However, unlike solid K₂C₂O₄, KCl showed a better extinguishing efficiency by Joseph [30]. Rosser [31] explained this chemical extinguishment effect of some salts by a volatility experiment using alkali metal salts, perfectly explained why the material is stable but also has a certain fire extinguishing efficiency.

DSC curve for KH₂PO₄ shows the two endothermic peaks and the corresponding TG curve has two weight loss platforms, which indicate that the thermal decomposition of KH₂PO₄ is completed in two steps. The first endothermic peak temperature is within 207.98–271.01 °C, with the peak temperature is 235.85 °C, weight loss rate is 6.9%, and endothermic enthalpy is 274.09 J g⁻¹. The second endothermic peak temperature is within 291.76–358.78 °C, whose peak temperature is 336.48 °C, weight loss rate is 7.64%, and endothermic enthalpy is 30.68 J g⁻¹. The TG curve shows that the thermal decomposition of KH₂PO₄ was completed at 360 °C, and no mass loss was observed at the test temperature of 800 °C. Du [32] also reported the decomposition process of KH₂PO₄ with two steps, one with the temperature range of 190–270 °C, and the other was 285–470 °C, which was not too different from the present study. Zhang [2] concluded the suppression efficiency of KH₂PO₄ by the covering effect of the stable white glassy state KPO₃, which generated from the decomposition of KH₂PO₄.

Mojumdar [33] declared that with the increase in temperature rate, the decomposition peak of potassium salts skewed to high temperature and becomes much sharper gradually. The decomposition peak temperature of potassium salts under different temperature rates varies. Decomposition activation energy of different potassium salts can be acquired by the Kissinger method. The Kissinger equation is as follows:

\[
\ln \left( \frac{\beta}{T'^{n}} \right) = \ln \left( \frac{A_{i}R}{E_{i}n} \right) - \frac{E_{i}}{R} \frac{1}{T'^{n}}, \quad i = 1, 2, \ldots, n
\]

In the equation, \( \beta \) is the heating rate, °C min⁻¹; \( T' \) is the peak temperature, K; \( A_{i} \) is the pre-exponential factor, s⁻¹; \( E_{i} \) is the activation energy, kJ mol⁻¹; \( R \) is the gas constant, J mol⁻¹ K⁻¹. The expression \( \ln \left( \frac{\beta}{T'^{n}} \right) \) to \( \frac{1}{T'} \) was mapped as the proper mechanism function with \( E_{i} \) as the slope and \( A_{i} \) as the intercept. The decomposition thermodynamic data of potassium salts are listed in Table 3.

### 3.3. Decomposition products analysis of potassium salts

The temperature of the heating tube was set according to the initial decomposition temperature of different potassium salts and was not higher than the limit temperature of the heating tube, more significantly, as 800 °C represented most of the actual flame temperature, this temperature existed in any set of experiments. Decomposition products were collected and analyzed, the experimental equipment was followed by Supplementary Fig. 7.

#### 3.3.1. The characterization of decomposition products under different temperature

Temperature of the tube type resistance furnace was controlled at 800, 900, and 1000 °C, respectively. Driven by air,
5% (mass concentration) ultrasonically atomized KCl water mist was added into the heating tube, the products are collected and the XRD analysis is shown in Fig. 2. Through contrast with PDF standard card, particles gained from ultrasonic atomization of KCl under different temperatures proved to be the diffraction peaks of KCl. XRD spectra of the product samples at different temperatures are similar with each other. Peaks for other impurity phases were absent, and the main diffraction peak is sharp, indicating the perfect crystal structure of the products. According to XRD spectra in Fig. 2, KCl particles could be gained from ultrasonic atomization of KCl at 1000 °C. SEM images of the product particles are shown in Fig. 3. Product particles at 800 °C were typical crystalline polymers with clear edges and corners. Although some particle clusters were present, the disparity remained good, and distinct cubic structure could be detected under 2500 amplifications. Crystals appeared, and the particle size was about 5 μm. Particles at 900 °C also showed good disparity, but particle size further increased, and the cubic structure gradually became rounder, indicating the spheroidization of the particles. Particle size at 1000 °C increased continuously, and particle clustering decreased. However, particle size increased to different extents, resulting in the poor particle uniformity. Particle edges and corners were significantly round, and spherical particles could be clearly observed under 8000 amplifications.

Driven by air, 5% (mass concentration) ultrasonically atomized water mist with other potassium salt additives was added into the heating tube, and the products were collected for XRD and SEM analysis. The characterization results of decomposition products by XRD under different temperature are shown in Table 4. XRD and SEM pictures are shown in supplementary materials.

As shown in Table 1 and Table 4, fire suppression efficiency and the behavior of potassium salts at high temperature depending on the anion of potassium salts. The decomposition products contained KOH and potassium oxides(K₂O), e.g. KO₂ and KO₃ in water mist with potassium salt additives with higher chemical fire extinguishing efficiency. Kong [34] and Liu [35] calculated the stability of alkali metal oxides through thermodynamics and showed that the final stable product in excess air could only be KO₂. However, large number of KO₃ existed in the decomposition products of water mist with KNO₃ additive in current research could be only from further oxidation of KO₂, which inferred the KO₂ might also be the active substance besides KOH during fire suppression. In addition, KOH has a good stability, that means KOH can not only act as an intermediate product, but also stabilize in the product because of the poor stability of intermediate product during the thermal decomposition of potassium salt. Chen [36] reported that within the range of inorganic compounds containing potassium ions, only KOH and K₂CO₃ had activity under low temperature which could relatively easy to hydrolyze KxOy compounds in water vapor environment. Decomposition products of water mist with KH₂PO₄ contains a lot of KPO₃, however, the reason for chemical extinguishing efficiency is not high partly due to higher stability of KPO₃, which causes it difficult to open up the chemical bond.

![Fig. 2. XRD results of heating product of water mist with 5% KCl.](image1)

![Fig. 3. SEM results of heating product of water mist with 5% KCl.](image2)
and releases potassium ions in the flame temperature; on the other hand, no KOH or K₂O₃ found in the products, which indirectly proved that KOH is a good active substance during fire extinguishing. There also has no KOH or K₂O₃ found in the products of water mist with KCl, however, due to the low melting point of KCl, K-Cl bond breaks in the form of melting, potassium ions are released and participate in fire extinguishing through chain termination reaction.

Characterization results by SEM shows that the particle size of the products increased in different degrees with the increase of the temperature, which is due to the influence of temperature on the formation and growth of crystal particles. The temperature changes the internal energy of the atom, that means particles with smaller average size can be obtained under low temperature for its beneficial to the formation of crystal particles, which is not conducive to the growth of crystal particles. The increase of temperature is equivalent to supply the kinetic energy of the crystal growth, which increases the mass transfer coefficient of the reaction and accelerates the growth of crystal particles, leading the particle size grow up [37].

### 3.3.2. The characterization of decomposition products under different concentration

The temperature is the main effect factor on decomposition of water mist with potassium salts, while the concentration may be also one of the factors on the size and uniformity of decomposition particle, the phenomenon which was found in many nano materials preparation process [38]. Guo [39] shows that the concentration could not change the kind of the products but the particle size. Theoretically, the solute content increases with increasing concentration under the same size of droplet. Once the droplet enters the reaction zone, the solvent evaporations and the solute separated out under the flame temperature. When the solvent evaporates completely, the temperature of the precipitated crystal rises rapidly to the ambient temperature and has a chemical reaction temperature condition. The higher concentration leads to the probability of particle collision and combination greatly increased, which inevitably leads to large particles. Large particles indirectly increase the decomposition time of the chemical particles, which is not conducive to the formation of chemical extinguishing active substances. In addition, the droplet diameter increases with the increase of the viscosity and surface tension of the solution, then, smaller particle size is conducive to product when the solution concentration is low [40].

SEM of the decomposition products of the K₂C₂O₄, CH₃COOK and K₂CO₃ aqueous solution under 800 °C are shown in Fig. 4.

As shown in Fig. 4, the morphology and particle size of the product is affected by concentration, and the general trend is that the particle size increases with the increase of solution concentration with more obvious agglomeration. When the mass fraction of the solution is less than 5%, the interface between particles is clear. The phenomenon of inter particle connection becomes obvious when the concentration increases, and finally agglomerated together to form a larger size particle. The experimental results show that, when the concentration is low, the dispersion and uniformity of the product particles is better, and the average particle size is relatively small. Hamins [41] reported that the time for full chemical reaction of alkali metal salt additives in flame reaction had a competitive relation with the residence time of alkali metal salt particles. If the residence time of alkali metal salt particles is shorter than the reaction time, then the fire-extinguishing agent cannot complete the chemical extinguishment. Small size is beneficial for chemical particle to use the least time to release the active substances. As shown in Table 1, K₂CO₃ has better suppression efficiency corresponding higher concentration than K₂C₂O₄ and CH₃COOK partly due to the smaller particle size under the same concentration. Similarly, the pyrolysis products of KNO₃, KCl and KH₂PO₄ solution at different concentrations have similar rules and no more details here.

### 3.4. Fire extinguishing mechanism analysis of water mist with potassium salts

Mitani [15] reported that when the droplet size is smaller than 5 μm, liquid drops serve as the carrier of powder rather than the extinguishing agent. After quick evaporation of liquid drops at flame temperature, micro solid powders or decomposition products of powders enter into the reaction zone of the diffusion flame. In this experiment, particle sizes of both ultrasonically atomized pure water and water mist with additives were found to be smaller than 5 μm by the laser particle analyzer. Therefore, water was the powder carrier in this experiment.

Based on the calculated results of thermoanalysis activation energy, the decomposition reactions of K₂C₂O₄ and CH₃COOK are sensitive to temperature, and the salts decomposed into K₂CO₃ immediately at flame temperature. The possible chemical reactions and reaction pathways of K₂CO₃ in vapor are as follows:

\[
\begin{align*}
\text{K}_2\text{CO}_3 & + \text{H}_2\text{O} = 2\text{KOH} + \text{CO}_2 \\
\text{K}_2\text{CO}_3 & = \text{K}_2\text{O} + \text{CO}_2 \\
2\text{KOH} & = \text{K}_2\text{O} + \text{H}_2\text{O} \\
\text{K}_2\text{O} & + \text{H}_2\text{O} = 2\text{KOH}
\end{align*}
\]

(1) (2) (3) (4)

Variations in standard Gibbs free energy of the above four reactions at 298–1400 K are shown in Fig. 5.

Fig. 5 shows that the chemical bond of K₂CO₃ is easier to break in the presence of vapor. KOH can be produced directly by Reaction (1) or gained indirectly by producing intermediate product K₂O (Reaction (2)) first and then through Reaction (4). Although the standard Gibbs free energy of Reaction (4) is smaller than 0, and Reaction (4) can be activated automatically without any external conditions, the reaction must first produce K₂O through Reaction (2). Provided that the standard Gibbs free energy of Reaction (2) is relatively large, and external reaction conditions are very strict,
the reaction producing KOH is apt to be Reaction (1), indicating the possibility of inducing the hydrolysis reaction of K₂CO₃ first than the decomposition reaction under vaporization conditions. This condition agrees with the mechanism of carbonate reduction by C of McKee et al. [42,43]. On the other hand, the standard Gibbs free energy of Reaction (4) is smaller than 0, which also implies the unstable existence of K₂O. K₂O is converted into KOH in the presence of H₂O. KOH existence was also verified by the XRD test.

The decomposition reaction (5) of KNO₃ includes the formation reaction (6) of KNO₂ and the decomposition reaction (7) of KNO₂:

\[
2\text{KNO}_3 = \text{K}_2\text{O} + \text{NO} + \text{NO}_2 + \text{O}_2 \quad (5)
\]

\[
2\text{KNO}_2 = 2\text{KNO}_2 + \text{O}_2 \quad (6)
\]

\[
2\text{KNO}_2 = \text{K}_2\text{O} + \text{NO} + \text{NO}_2 \quad (7)
\]

The standard Gibbs free energy of KNO₂ at temperatures higher than 298 K is inapplicable [23]. Therefore, thermodynamic calculation was accomplished according to Reaction (5). Possible reaction of KNO₃ in the presence of vapor is as follows:

\[
2\text{KNO}_3 + \text{H}_2\text{O} = 2\text{KOH} + \text{NO} + \text{NO}_2 + \text{O}_2 \quad (8)
\]

Variations in the standard Gibbs free energy of Reactions (5) and (8) at 298–700 K are shown in Fig. 6.

In the presence of vapor, KNO₃ easily decomposes into K₂O, which can automatically produce KOH through hydrolysis reaction. Activity of KNO₂ results from the decomposition reaction (5), and KNO₂ is a possible intermediate product of the reaction. Although thermodynamic calculation shows that Reaction (5) has high ΔG°, its existence can be proven by thermoanalysis. Based on thermodynamic calculation, Liu [35] pointed out that KO₂ is the stable product of K in excessive air and can react with excessive air to form KO₃. Hence, the XRD test revealed that the final products of the complicated decomposition reaction of KNO₃ under the existence of vapor are mixtures of KOH, KO₂, and KO₃.
The possible reaction of KCl in the vapor atmosphere is as follows:

\[ \text{KCl} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{HCl} \]  \hspace{1cm} (9)

KOH was not observed in the XRD analysis of the product, indicating that the reaction conditions are strict. Based on the thermoanalysis, solid KCl melts when the temperature exceeds 1044 K, which can further accelerate the hydrolysis reaction of KCl. On the other hand, provided that alkali halide has high saturated vapor pressure [10], some accelerated hydrolysis reactions may be attributed to gaseous hydrolysis. KOH is the only possible product in KCl activation, which is consistent with the research conclusions of McKee and Verra et al. [42,43]. Verra believed that K\(_2\)O was the product of the first-step KCl reaction under the existence of gaseous vapor, but the compound can only be the intermediate product under the existence of vapor. Hydrolysis of KCl requires high temperature. Given the high saturated vapor pressure of KCl, evaporation of KCl accelerates its hydrolysis reaction and offsets the disadvantage of low burnt temperature.

Based on thermoanalysis and XRD test, reaction products of KH\(_2\)PO\(_4\) under the existence of vapor were stable and were composed mainly of glassy KPO\(_3\). No KOH was found.

Equilibrium calculation of products of CH\(_4\)/air burning system with 5% potassium salt solutions was implemented by HSC Chemistry 6. Results are shown in Figs. 7 and 8.

Figs. 7 and 8 show that KOH exists as equilibrium products of K\(_2\)C\(_2\)O\(_4\), CH\(_3\)COOK, K\(_2\)CO\(_3\), and KNO\(_3\) in the flame reaction zone. We speculated that KOH is the key component in producing extinguishing active substances. At the same time, KNO\(_3\) can reduce the free radical OH concentration significantly. The SEM experiment showed that under high temperature, pyrolysis products of KNO\(_3\) follow a spheroidization trend, which is beneficial in developing the extinguishing performance and offsetting the disadvantage of lower KOH percentage than K\(_2\)CO\(_3\). Moreover, the extinguishing performance of KNO\(_3\) observed in the cup burner experiment was basically consistent with those of K\(_2\)C\(_2\)O\(_4\), CH\(_3\)COOK, and K\(_2\)CO\(_3\). The chemical extinguishing performance of KCl was caused by the high percentage of KCl in the equilibrium products, indicating that KCl has certain volatility at high temperature, and its chemical extinguishing performance was influenced to a large extent by the few KOH produced by gaseous hydrolysis reaction.

In previous studies, Jensen and Jones [44] had proposed the mechanism of potassium salts to inhibit fire radical as follows, which M is a third body participates in chain reactions:

\[ \text{KOH(g)} + \text{H} \rightarrow \text{H}_2\text{O(g)} + \text{K} \]  \hspace{1cm} (10)

\[ \text{K} + \text{OH} + \text{M} \rightarrow \text{KOH(g)} + \text{M} \]  \hspace{1cm} (11)

Hynes [45] and Slack [19] showed that the suppression kinetic mechanism containing potassium salts should also contain XO and XO\(_2\), revealed the possible reaction path and holed that the importance of the reaction (12) is equivalent to the reaction (11).

\[ \text{K} + \text{O}_2 + \text{M} \rightarrow \text{KO}_2\text{(g)} + \text{M} \]  \hspace{1cm} (12)

\[ \text{KO}_2\text{(g)} + \text{H} \rightarrow \text{KO(g)} + \text{OH} \]  \hspace{1cm} (13)

Williams and Fleming [46] considered all the researchers and put forward a suppression kinetic mechanism model containing sodium species:
Considering the similarity of sodium and potassium, the active substances from the decomposition products of water mist with potassium salts for chemical kinetics mechanism should include at least the species KOH, KO2, KO and K, and this conclusion can be expressed by Fig. 9.

Potassium salt with oxygen containing can be used to provide active substances such as KOH and KxOy in fire extinguishing under the condition of water vapor. However, for the KCl-water mist, Zheng [4] pointed out the promotion of suppression might from Cl2 radical which produced by Cl radical from KCl at flame temperature.

Then, as an inhibitor, Wilson [47] reported the chemical mechanism path by reactions (18)–(20).

$$\text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl} \quad (18)$$

$$\text{HCl} + \text{H} \rightarrow \text{H}_2 + \text{Cl} \quad (19)$$

$$\text{H} + \text{OH} + \text{Cl} \rightarrow \text{H}_2\text{O} + \text{Cl} \quad (20)$$

4. Conclusions

The current research enriches the database of minimum fire extinguishing concentration of water mist with some potassium salts. The active substances from decomposition in flame temperature of water mist with some potassium salts are creatively obtained by thermoanalysis experimental method which has more reliability and accuracy, and the quantitative analysis of active substances in fire suppression is obtained through thermodynamics method by HSC CHEMISTRY 6. The main conclusions of the present research are:

(1) Potassium salts chosen from current research can improve the extinguishing performance of pure water, and K2CO3 has the most benefit with the improving rate of 37.6%, 47.2% and 64.8% which the mass percent is 1%, 2% and 5%, respectively, followed by K2C2O4, CH3COOK, KNO3, KCl and KH2PO4.

(2) Active substances that participate in extinguishment under gas vapor were consistent and unrelated with the type of potassium salts used. Therefore, extinguishing performance of different potassium salts is due to the activation behaviors of potassium salts under gasification conditions. Potassium salts, which have high extinguishing performance, produce KOH during flame chemical reactions. As the key component of activation of potassium salts, KOH can further react with free radicals in flames to produce extinguishing active substances.

(3) Higher fire extinguishing efficiency corresponds to more active substances. The main potassium salts such as K2CO3, KNO3, KCl and KH2PO4 provides active substances KOH 4.85%, 1.3%, 5.13% and 7.16% respectively, which indicates the influence of anions on the fire extinguishing efficiency.

Furthermore, the MEC of some other kinds of potassium additives should be obtained, and for the engineering application of water mist with potassium salt additives, physical and chemical properties of fire extinguishing agent, mostly the toxicity, for example, the emission of Cl, P and N species whether be harmful to firefighters or environment should be the further work.
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Appendix A. Supplementary material

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