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Analysis of safety characteristics of coal-based aviation kerosene

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Abstract: The risk and thermal safety characteristics of GX kerosene, HX kerosene and WX kerosene are studied. Firstly, the explosion lower limits of three kinds of kerosene steams are tested by using the self-made explosion limit measuring system. Then differential scanning calorimeter (DSC) is employed to perform linear heating experiment on kerosene to analyze its thermal decomposition characteristics. The pyrolysis kinetic parameters of three kinds of kerosene are calculated based on the thermal dynamic methods. The experimental results show that the flash point and lower explosion limit of GX kerosene are relatively low. The DSC test shows that the lowest initial decomposition temperature of HX kerosene is 116.5 ℃. According to pyrolysis kinetics calculation, the T_{D24} and apparent activation energy of HX kerosene are the minimum. ARC test shows that GX kerosene has the worst thermal stability under the adiabatic condition. The high temperature stabilities of the three kinds of kerosene all meet the requirements. On the whole, GX kerosene has the highest hazard, and HX kerosene has the lowest thermal safety. The accumulation of heat should be prevented during the storage and transportation of kerosene. This study provides the crucial safety characteristics data of coal-based aerospace kerosene-based, and provides technical support for engine reliability growth and performance improvement.

Key words: aerospace kerosene; hazard; pyrolysis kinetics; thermal safety

0 Introduction

The development of space technology in the future is focused on the liquid oxygen kerosene engine and heavy launch vehicles, and the demand for aerospace kerosene as its main propellant is increasing[1-5]. In a variety of propellants, liquid oxygen/kerosene propellant with advantages of low cost, high density, good storage performance, environmental protection and non-toxic, has become the focus of research and development in some space powers[6-9]. In large launch vehicles, rocket kerosene accounts for 70% to 90% of the takeoff weight. Therefore, the cost and performance of kerosene are of great significance to launch vehicles[10].

Kerosene is an essential fuel for rocket propulsion, and high-energy/insensitivity is an important direction for the future development of energetic materials, so high-energy kerosene has been the focus of research in the field of aerospace propulsion fuel. In the complex space propulsion system, fuel is not only the power source but also the primary hazard source. Therefore, the safety of fuel has always been of great concern. The variation law of physicochemical properties of coal-based aerospace kerosene and petroleum-based aerospace kerosene blended in different proportions is studied[11]. By blending different proportions of the two kerosenes and measuring the core indexes, it is found that the two kerosenes can be blended arbitrarily and the various physicochemical properties meet the requirements of use. The inhibitory effect of perfluorohexanone on the combustion of aviation kerosene is investigated, and it is found that with the increase of the concentration of perfluorohexanone in the air, the combustion flame of aviation kerosene experiences a slow increase and then a rapid decrease[12]. It shows that there is a transition from promotion to inhibition of the effect of perfluorohexanone on kerosene combustion at different concentrations. The vacuum specific

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impulse, pulse operation performance and response performance of coal-based high energy kerosene engine are studied[13]. The results show that the engine has reliable ignition and stable combustion performance by using the coal-based high energy kerosene. The pulse operation performance, starting and shut off response performance could satisfy the engineering application requirements. The vacuum specific impulse is 7 s higher than that of the basic rocket kerosene engine. The influence of ethanol addition on the combustion rate of RP-3 aviation kerosene premixed flame is investigated[14]. The results indicate that the combustion rate of ethanol/RP-3 premixed flame increases with ethanol addition. The effect of initial temperature and pressure on the lower explosion limit of RP-3 aviation kerosene steam is studied[15]. It is found that the lower explosion limit decreases with increasing initial temperature but increases with the increase of initial pressure.

Theoretically, the composition of coal-based space kerosene is dominated by cycloalkanes, supplemented by paraffin, and contains a minimal amount of aromatic hydrocarbons with very stable chemical properties[16-20]. In terms of application, as new high-energy kerosene, its safety assessment should be stricter than that of conventional fuels. The different environments will have an important influence on the flash point, thermal sensitivity and stability of kerosene. Considering the operating conditions of kerosene and the gaps in this research field in China, it is urgent to conduct research on important safety parameters of coal-based aviation kerosene. It provides data support for the safety evaluation of coal-based aerospace kerosene and improves the essential safety of high-value rocket launch platforms. This paper is oriented to the application environment of rocket engine engineering, combined with the operating conditions of kerosene. The safety characteristics test method in harsh environments is established through the research on the risk and thermal safety risk of coal-based aerospace kerosene. The obtained safety characteristic data of coal-based aerospace kerosene can provide essential references for engine reliability growth and performance improvement.

1 Experiment

1.1 Materials

Three typical aviation kerosene samples of GX kerosene, HX kerosene and WX kerosene are selected. Coal-based aerospace kerosene contains double cycloalkanes, a small number of monocyclic alkanes and tri cycloalkanes, etc. Combining the molecular formula and content of each component, the equivalent molecular weight of the sample is about 160－170. The density of space kerosene is about 0.80 g/cm^3－0.85 g/cm^3. Due to the thermal expansion of aerospace kerosene, its density tends to decrease with the increase in temperature. The boiling point ranges from 150 ℃ to 280 ℃.

1.2 Experimental setup and method

1.2.1 Hazardous study of coal-based aerospace kerosene

In this study, based on three kinds of aviation kerosene samples, their hazardous parameters such as flash point, ignition point and lower limit of the explosion are measured. The detailed measurement steps and standards are described as follows.

The open cup flash point and ignition point of aerospace kerosene are measured according to GB/T3536 Determination of Flash Point and Ignition Point of Petroleum Products Cleveland Open Cup Method. Using YP1001B-Ⅱ petroleum products ignition point and ignition point tester, the inner diameter of the Cleveland oil cup is (62.5 ± 0.5) mm, and the power of heating the electric furnace is 400 W. The test is conducted at a frequency of scanning twice per minute until the predetermined test temperature, then the open cup flash point and ignition point are measured. The closed cup flash point is measured by Miniflash FLP closed cup flash point automatic tester. The experiment is conducted twice to take the average value.

The lower explosion limit test device is shown in Fig. 1, mainly composed of a shock tube, ignition device, vacuum pump, pressure gauge, heating device, ball valve, data acquisition system, etc. The main part of the device is a stainless steel shock tube equipped with a pressure sensor and a K-type thermocouple. The shock tube is evenly wrapped with a circle of the heating belt, the outer layer of insulation asbestos, and wrapped with insulation tape to ensure that the temperature inside the shock tube is maintained at 120 ℃, enabling the kerosene added into the tube to evaporate into kerosene steam. Then different amounts of kerosene are added to the shock tube through the feeding port with a syringe and waited for 15 min to ensure that the kerosene in the tube is vaporized entirely into kerosene steam, filling the whole tube uniformly. Finally, the critical concentration of kerosene steam explosion is measured by igniting kerosene steam with different volume fractions using the chemical ignition head.

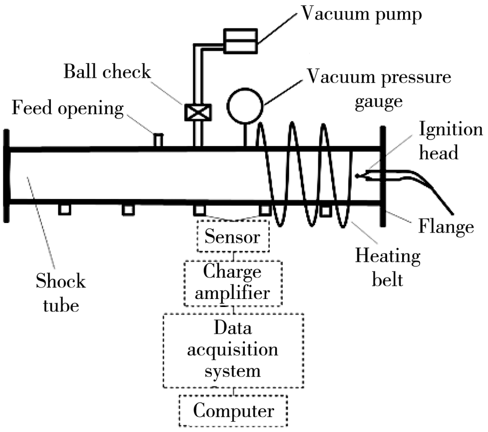


Fig. 1 Explosion limit test device

1.2.2 Thermal safety risks of coal-based aerospace kerosene

The heat flow differential scanning calorimeter (DSC-1) produced by METTLER TOLEDO is used for the DSC test, with a calorimetric sensitivity of 0.04 mW, a test temperature range of −35 ℃ to 500 ℃, and a heat flow range of ±350 mW. The test sample tank is a disposable perforated crucible, the atmosphere is high-purity nitrogen, and the heating rate includeds 2 ℃/min, 4 ℃/min, 8 ℃/min and 10 ℃/min, with a temperature range of 30 ℃ to 500 ℃.

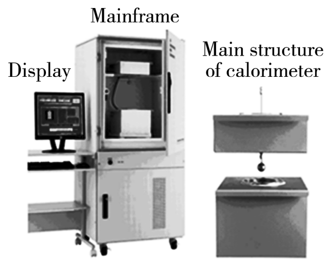


Fig. 2 ARC experimental device

The thermal decomposition characteristics of kerosene under adiabatic conditions are studied by using an accelerating rate calorimeter (ARC) manufactured by THT UK to obtain the law of kerosene pressure and temperature variation with time. The kinetic parameters of kerosene thermal analysis under adiabatic conditions are obtained by processing ARC test results. The test model for kerosene samples is heat-wait-search, the detection sensitivity is 0.02 ℃/min, the detection temperature range is 30 ℃−400 ℃, the temperature rise step is 5 ℃, and the waiting time is 10 min. The test sample spheres are Ti with a mass of 6.113 g−6.792 g. The injection mass of each kind of kerosene is 2.00 g. Fig. 2 shows the ARC test device.

2 Results and discussion

2.1 Hazardous study of coal-based aerospace kerosene

The flash point is the lowest temperature at which a liquid is vaporized and ignited by a specific ignition source under certain conditions. It is significant for producing, storing, transporting, and using combustible and flammable liquids[21-23]. The lower the flash point, the greater the risk of fire and explosion, so it is an important index of the safety of liquid propellants. The ignition point refers to the minimum temperature required to apply an external heat source to cause the surface of a substance to ignite and burn continuously for a certain period under specified test conditions[24]. Therefore, the lower the ignition point of kerosene, the more likely fire accidents will occur. Experimental measurement results are shown in Fig. 3.

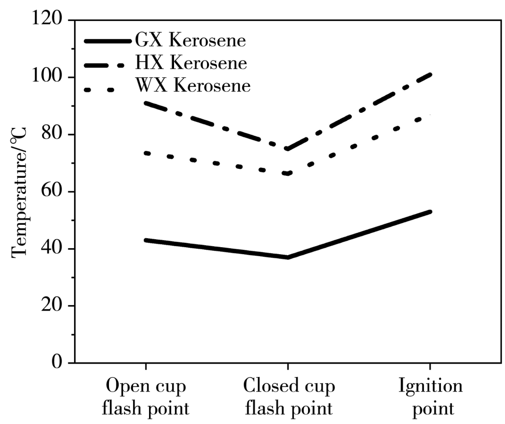


Fig. 3 Kerosene flash point and ignition point

The results show that the open cup flash point of GX kerosene is 43 ℃, the closed cup flash point is 37 ℃, and the ignition point is 53 ℃. HX kerosene's open cup flash point is 91 ℃, the closed cup flash point is 75 ℃, and the ignition point is 101 ℃. The flash point of WX kerosene is 73.5 ℃ in the open cup, 66.3 ℃ in the closed cup, and 87 ℃ in the ignition point. From the flash point and ignition point analysis, it can be seen that GX kerosene is the most dangerous, followed by WX kerosene, and HX kerosene is the least dangerous. In the process of transportation and storage, special attention should be paid to the safety of GX kerosene, whose flash point is less than 60 ℃, which is flammable.

The lower explosion limit characteristic is crucial for the safety of kerosene steam. The lower the explosion limit of kerosene steam, the more chances of its explosion, indicating that the greater the danger, and a slight leakage of kerosene steam could cause an explosion. The experimental results are shown in Fig. 4.

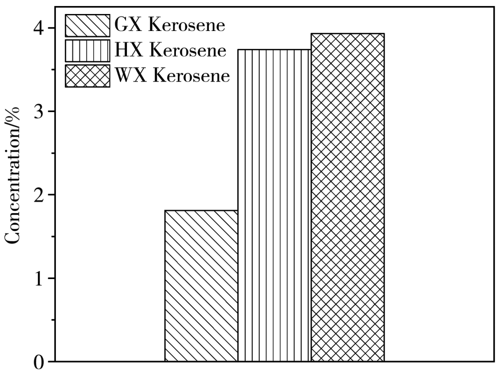


Fig. 4 Lower limit of kerosene explosion

As seen in Fig. 4, the lower explosion limit of GX kerosene, HX kerosene and WX kerosene steam are 1.81%, 3.74% and 3.93%, respectively. The lower explosion limit of GX kerosene is the lowest among the three kinds of kerosene, while HX kerosene and WX kerosene have similar explosion lower limits. It indicates that GX kerosene is one of the three with a slightly wider explosion limit and a higher possibility of explosion.

2.2 Pyrolysis kinetics of coal-based aerospace kerosene

Fuel's heat transfer, safety and storage performance are affected by thermal stability. DSC is used to study the heat absorption and exothermic effect of three kinds of kerosene with temperature change to obtain the thermal stability of three kinds of kerosene. The experimental data of initial decomposition temperature and heat release at different heating rates are obtained. The kinetic parameters of three kerosene samples, including pre-exponential factor and expression activation energy, are calculated by DSC curves under different temperature rise rates. In this paper, the Friedman method in AKTS software is used to calculate the kinetics of related materials, and the TMR_{ad} and T_{D24} of three kinds of kerosene are predicted on the basis.

2.2.1 DSC data analysis

The test results of three kerosene samples at different temperature rise rates are summarized in Fig. 5, and the dynamic scanning results are shown in Table 1.

Table 1 Dynamic scanning results

(a) GX kerosene

Temperature rise rate/(℃ · min^{-1})	Sample quality/mg	Peak 1		Peak 2	
		Starting temperature/℃	Heat release/(J · g^{-1})	Starting temperature/℃	Heat release/(J · g^{-1})
4	1.37	177.95	330	386.33	1 115
8	1.42	222.90	350	386.90	1 075
10	1.41	180.23	351	392.24	1 194

(b) HX kerosene

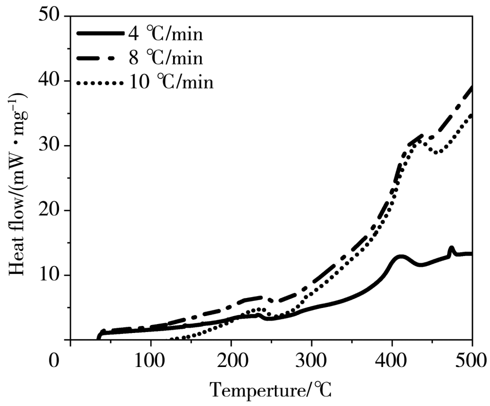
Temperature rise rate/(℃ · min^{-1})	Sample quality/mg	Peak 1	
		Starting temperature/℃	Heat release/(J · g^{-1})
4	1.37	116.47	648
8	1.40	119.64	628
10	1.41	120.80	642

(c) WX kerosene

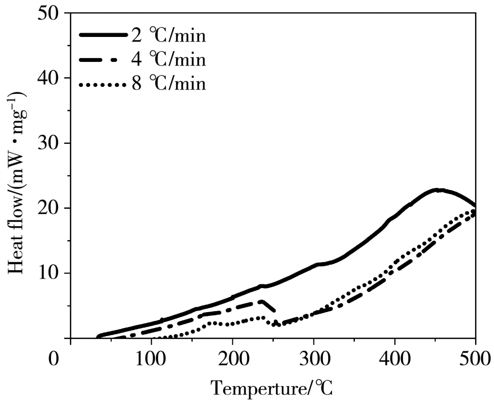
Temperature rise rate/(℃ · min^{-1})	Sample quality/mg	Peak 1		Peak 2		Peak 3	
		Starting temperature/℃	Heat release/(J · g^{-1})	Starting temperature/℃	Heat release/(J · g^{-1})	Starting temperature/℃	Heat release/(J · g^{-1})
2	1.35	162.78	168.1	274.42	325.3	418.37	238.5
4	1.37	167.35	168.4	277.38	298.8	419.13	240.1
10	1.35	178.62	158.8	297.02	280.7	418.30	219.1

Note: The starting temperature in the table is the temperature at which the exothermic curve is deviated from the baseline.

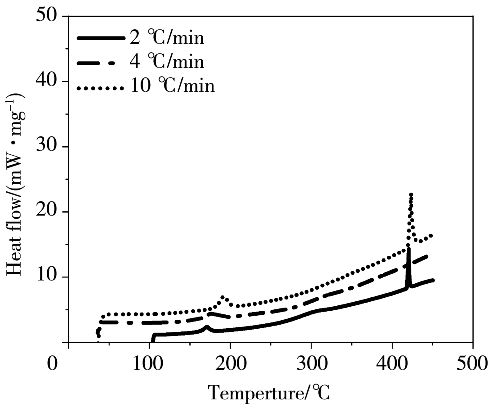
As shown in Fig. 5, with the increase in heating rate, the exothermic peaks of the three kinds of kerosene all move towards high temperatures, showing the same pattern of change. As the heating rate of the instrument increases, the heat exchange process between kerosene and the environment is shortened, and the thermal hysteresis phenomenon increases the decomposition temperature of kerosene. It should be pointed out that the decomposition process of kerosene is exothermic because aerospace kerosene contains multiple tension rings, and once decomposition occurs, a large amount of energy accumulated within molecules is released, leading to exothermic phenomena. The three types of kerosene have slightly different structures. 2%—4% active additives are added to GX kerosene to improve its activity and make GX kerosene more active chemically. 2%—4% passivation additives are added to HX kerosene to have an inhibiting effect and enhance the safety of HX kerosene. 2%—4% alkane additives are added to WX kerosene, which makes the chemical properties of WX kerosene more stable.



(a) GX Kerosene



(b) HX Kerosene



(c) WX Kerosene

Fig. 5 DSC test results at different heating rates

It resulted in different numbers of exothermic peaks in the decomposition of the three kerosenes, with GX kerosene showing two exothermic peaks, HX kerosene one exothermic peak and WX kerosene three exothermic peaks. In addition, from the analysis of the peak pattern of kerosene decomposition, it can be seen that the three kinds of kerosene decomposition are different in intensity, among which HX kerosene decomposes most vigorously, followed by WX kerosene, while GX kerosene decomposes more moderately.

Under different heating rates, the initial temperature of the first exothermic peak of GX kerosene is 177.95 ℃—222.90 ℃, and the average heat release is 343 J/g. The initial temperature of the second exothermic peak is 386.33 ℃—392.24 ℃, and the average heat release is 1 128 J/g. The initial exothermic peak temperature of HX kerosene is 116.47 ℃—120.80 ℃, and the average heat release is 639 J/g. The initial temperature of the first exothermic peak of WX kerosene is 162.78 ℃—178.62 ℃ with an average heat release of 171 J/g, the initial temperature of the second exothermic peak is 274.42 ℃—297.02 ℃ with an average heat release of 301 J/g, and the initial temperature of the third exothermic peak is 418.30 ℃—419.13 ℃ with an average heat release of 232 J/g. According to the first exothermic peak of kerosene to analyze its safety, HX kerosene has the lowest initial decomposition temperature and the highest possibility of accidents among the three kinds of kerosene.

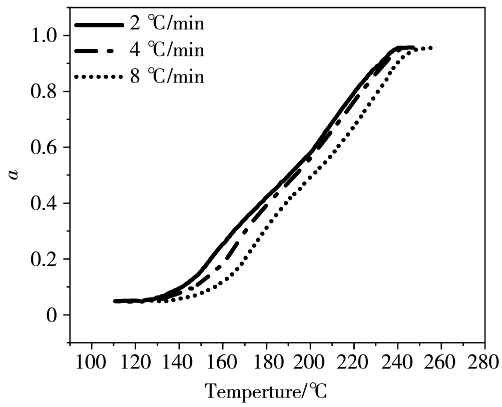
2.2.2 Thermal analysis kinetics

The equal conversion method is commonly used in the kinetic calculation. The Friedman method is the most common differential method for equal conversion, which is suitable for dynamic and isothermal testing modes. Its basic equation is

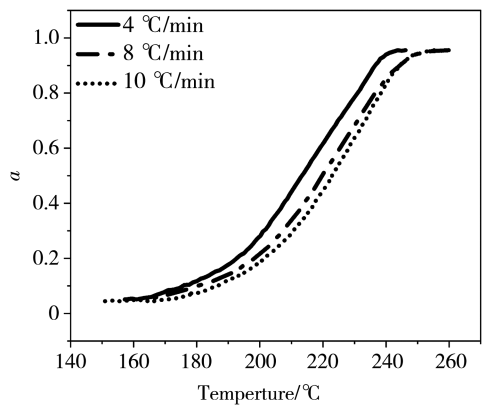
$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,i}=\ln[f(\alpha)A_\alpha]-\frac{E_\alpha}{RT_{\alpha,i}}, \tag{1}$$

where $(\mathrm{d}\alpha/\mathrm{d}t)_\alpha$ is the reaction rate, s^{-1}; α is conversion rate; A_α is the pre-exponential factor, s^{-1}; $f(\alpha)$ is the mechanism function; E_α is the activation energy, kJ/mol; R is the ideal gas coefficient, J/(mol · K); T is the temperature, K. The subscript i denotes different temperature control methods. The subscript α represents the corresponding value at a certain conversion rate α. For isothermal reactions, i corresponds to different isothermal temperatures. i corresponds to different rates of temperature rise for linear processes. At a certain conversion rate α, E_α can be obtained from the slope of the line obtained by fitting the data from $\ln(\mathrm{d}\alpha/\mathrm{d}t)_{\alpha,i}$ and $1/T_{\alpha,i}$ using the least square method. Finally, a series of E_α corresponding to α can be obtained.

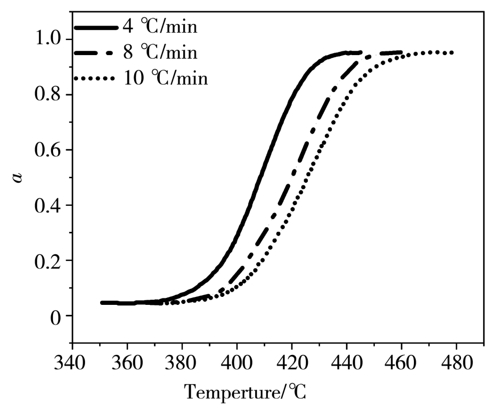
Fig. 6 shows the results of kinetic calculations based on the Friedman method for different exothermic peaks of three kinds of kerosene. It can be obtained that the decomposition heat of the first and second peaks of GX kerosene are (358±21) J/g and (1 165±44) J/g at three temperature rise rates. The decomposition heat of HX kerosene at three temperature rise rates is (729 ± 163) J/g. The decomposition heat of the first, second and third peaks of WX kerosene are (176. 335±5. 816) J/g, (176. 335±5. 816) J/g and (238. 191±5. 543) J/g at three temperature rise rates, respectively. Overall, the decomposition heat of the second peak of GX kerosene is obviously higher, indicating that more heat is released during decomposition.



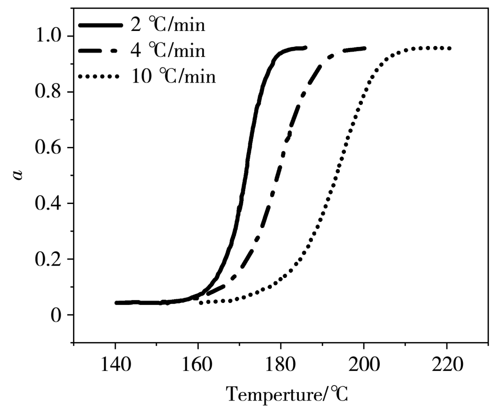
(a) HX Kerosene peak 1



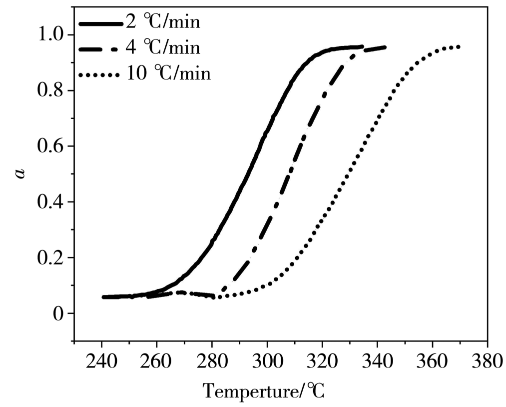
(b) GX Kerosene peak 1



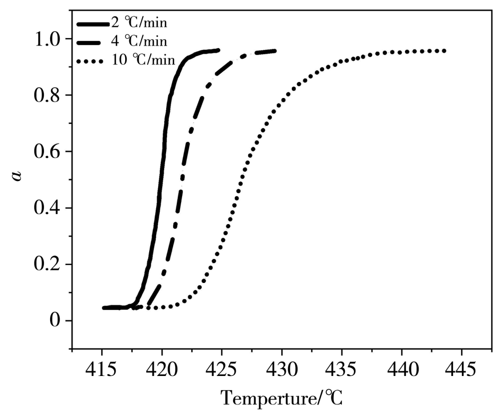
(c) GX Kerosene peak 2



(d) WX Kerosene peak 1



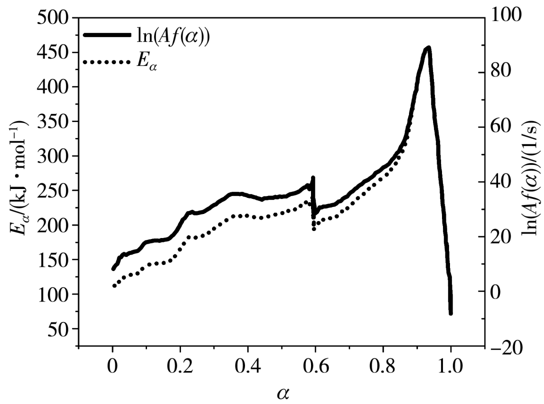
(e) WX Kerosene peak 2



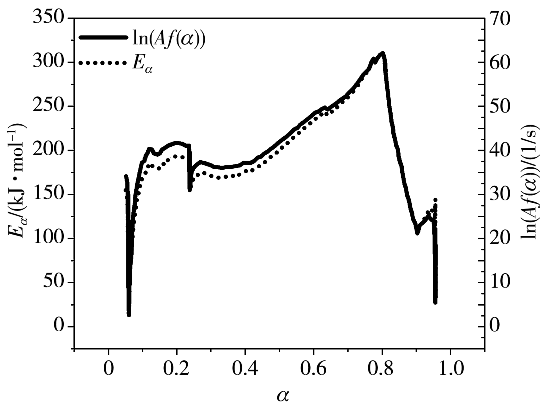
(f) WX Kerosene peak 3

Fig. 6 Summary of fitting results and measured results of reaction rate

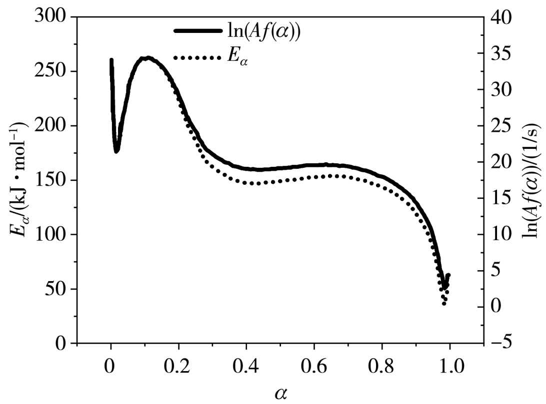
Fig. 7 shows the relationship curves of E_a and $\ln(Af(\alpha))$ with conversion rate α calculated by Friedman method. The analysis shows that the thermal decomposition process of GX kerosene is complex, and there are two-step reactions. The apparent activation energy of the first exothermic peak increases first and then decreases with the increasing conversion rate. When the conversion rate reaches 0. 2, the apparent activation energy of the first step reaction drops abruptly. The decomposition of intermediate products affects the exothermic reaction of the second step.



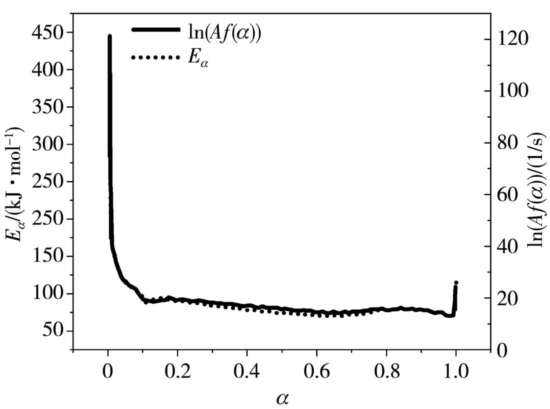
(a) HX Kerosene peak 1



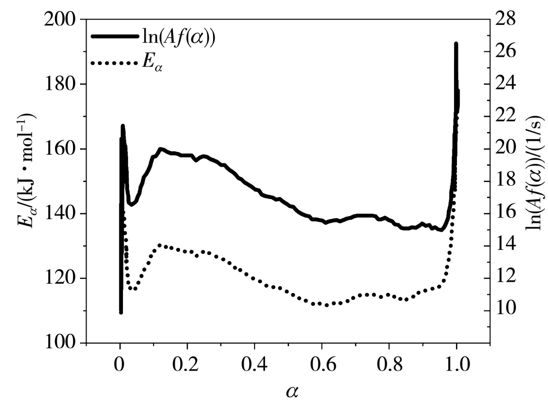
(b) GX Kerosene peak 1



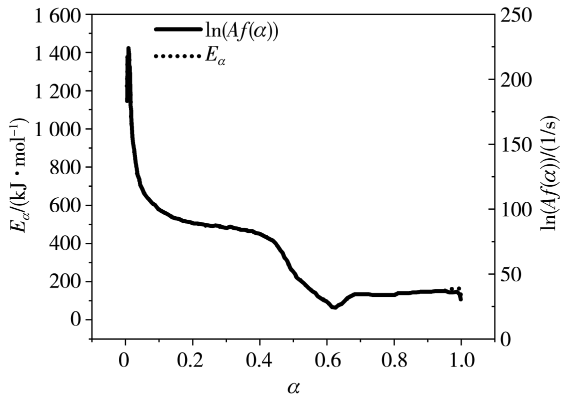
(c) GX Kerosene peak 2



(d) WX Kerosene peak 1



(e) WX Kerosene peak 2



(f) WX Kerosene peak 3

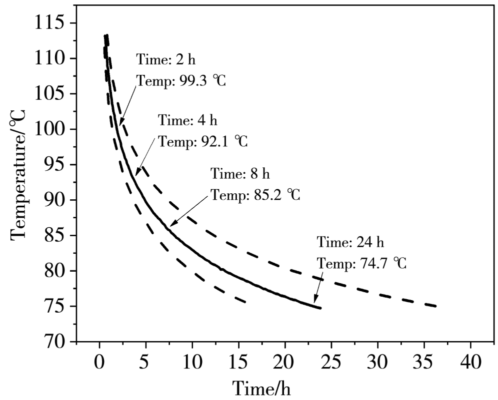
Fig. 7 Relationship between E_α and ln($Af(\alpha)$) calculated and conversion rate α

The heat released from the second step reaction gradually increases, and the apparent activation energy rises, at which time the proportion of the second step is dominant. The heat released from the second step reaction gradually increases, and the apparent activation energy rises, at which time the proportion of the second step is dominant. When the conversion rate reaches 0.85, the apparent activation energy is the highest, then the reaction approaches the end, and the activation energy decreases gradually. The apparent activation energy of the second exothermic peak decreased with the increase of the conversion rate. At the beginning of the reaction, the activation energy is the highest at a conversion rate of 0.1 and then gradually decreases. The apparent activation energy decreases rapidly between 0.1 and 0.3 and then tends to be stable, indicating that the reaction is relatively stable at this stage. The thermal decomposition reaction of HX kerosene also has two steps. On the whole, the apparent activation energy increases gradually as the conversion rate rises. When the conversion rate reaches 0.6, the apparent activation energy of the first step reaction drops abruptly. When the conversion rate is between 0.6 and 0.9, the increasing rate of activation energy is obviously higher than that before 0.6. The intermediates generated from the first step contribute to the second step reaction. The apparent activation energy reaches the maximum at a conversion rate of 0.9. The apparent activation energies of the three peaks of WX kerosene thermal decomposition show a downward trend with the conversion rate increase, indicating that the reaction process is relatively simple. It should be noted that the third exothermic peak, where the apparent activation energy drops significantly at the conversion rate of 0.45—0.60, reveals that some macromolecular alkanes in kerosene have reacted completely. The apparent activation energies of the first exothermic peak of three kinds of kerosene are compared and analyzed. HX kerosene has the lowest activation energy, followed by WX kerosene, and GX kerosene has the highest activation energy. The results show that the energy required for HX kerosene to change from a normal state to an active state prone to biochemical reaction is the least among the three kinds of kerosene. Therefore, HX kerosene has the lowest safety from activation energy analysis.

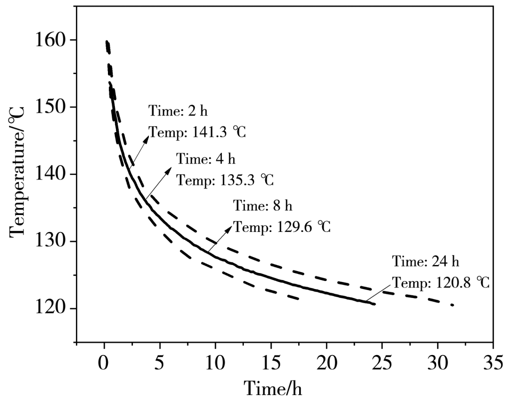
2.2.3 Calculation of adiabatic induction period

Thermal runaway occurs when the exothermic rate of a reaction system is greater than the heat transfer rate. An important parameter of runaway reaction is the arrival time of the maximum temperature rise rate under adiabatic conditions, also known as the adiabatic induction period, or the arrival time of the maximum reaction rate under adiabatic conditions, i.e., TMR_{ad}, which can also be considered as the time to take emergency measures before a loss of control occurs. T_{D24} represents the temperature corresponding to the time to reach the maximum reaction rate of 24 h under adiabatic conditions. Here the relationship between TMR_{ad} and the initial temperature of the substance is determined based on the kinetic parameters obtained by AKTS software. The adiabatic temperature profiles for three kinds of kerosene are shown in Fig. 8.

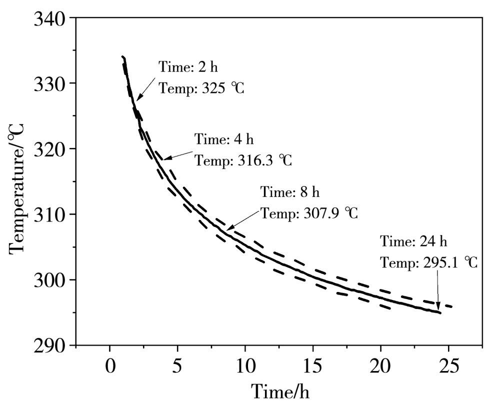
In the calculation of the adiabatic induction period, the data used is from DSC experimental curves at different heating rates. The heat release of each curve is different, so the heat release has a certain range, as shown in Table 1. As seen in Fig. 8, the slope of the curve tends to increase when the initial temperature of the three kinds of kerosene is higher than T_{D24}, showing that the adiabatic induction period is less affected by temperature at high temperatures.



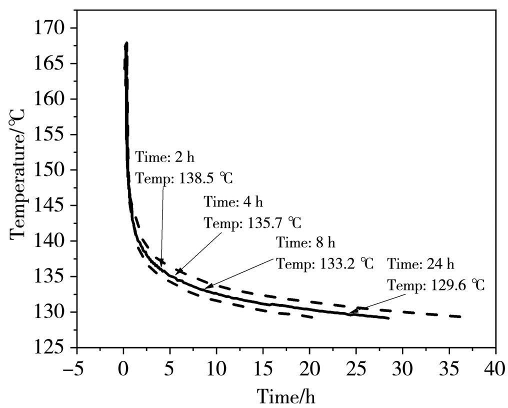
(a) HX Kerosene peak 1



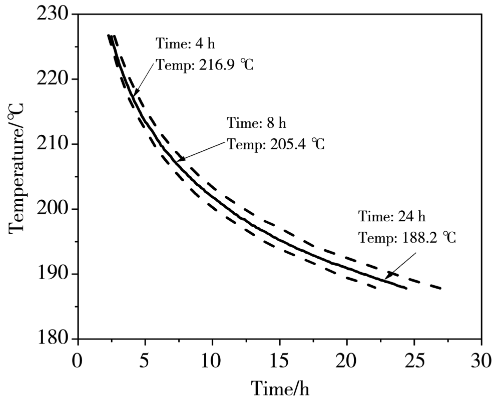
(b) GX Kerosene peak 1



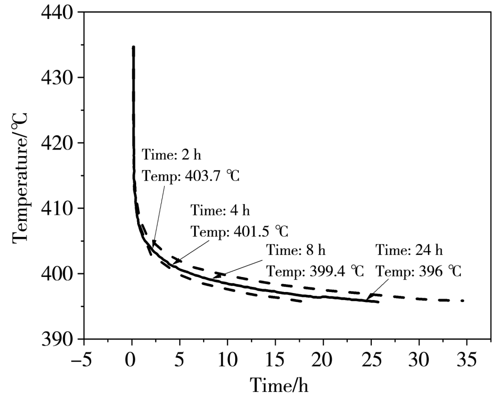
(c) GX Kerosene peak 2



(d) WX Kerosene peak 1



(e) WX Kerosene peak 2



(f) WX Kerosene peak 3

Fig. 8 Adiabatic temperature history of three kinds of kerosene in different induction periods

When the initial temperature is lower than T_{D24}, the curve's slope is smaller, indicating that the adiabatic induction period is greatly affected by temperature at low temperatures. Furthermore, the T_{D24}, T_{D4} and T_{D8} of the first exothermic peak of GX kerosene are 120.8 ℃, 135.3 ℃ and 129.6 ℃, respectively. T_{D24}, T_{D4} and T_{D8} of the second exothermic peak are 295.1 ℃, 316.3 ℃ and 307.9 ℃, respectively. The T_{D24}, T_{D4} and T_{D8} of HX kerosene are 74.7 ℃, 92.1 ℃ and 99.3 ℃, respectively. For the WX kerosene, the T_{D24}, T_{D4} and T_{D8} of the first exothermic peak are 129.6 ℃, 135.7 ℃ and 133.2 ℃, respectively. The T_{D24}, T_{D4} and T_{D8} of the second exothermic peak are 188.2 ℃, 216.9 ℃ and 205.4 ℃, respectively. The T_{D24}, T_{D4} and T_{D8} of the third exothermic peak are 396.0 ℃, 401.5 ℃ and 399.4 ℃, respectively. It can be obviously seen that the T_{D24} of the three kinds of kerosene is lower than the initial decomposition temperature mentioned in Table 1.

In summary, slowing thermal decomposition will occur if the temperature is lower than the initial decomposition temperature during the storage of coal-based aerospace kerosene. If the heat generated cannot be diffused, it will gradually accumulate, leading to safety risks. Comparing the T_{D24} of the first peak of the three kinds of kerosene, it can be seen that the T_{D24} of HX kerosene is the lowest, followed by GX kerosene, and T_{D24} of WX kerosene is the highest, indicating that HX kerosene has the lowest thermal safety among the three kinds of kerosene. Therefore, the storage of kerosene should be avoided in an adiabatic environment or in a large mass pile to prevent the heat accumulation. For safety, the storage environment of kerosene should be kept ventilated, and the adiabatic induction period should be considered as an important safety parameter.

2.2.4 Self-accelerated decomposition temperature

Combined with kinetic parameters, the SADT of the three kerosene is calculated by using the DSC experimental curve in Fig. 5 and the data in Table 1. SADT is the self-accelerating decomposition temperature, which is an important indicator for the safe management of chemical substances in storage and transportation. SADT can represent the thermal safety characteristics of the packaging, which is not only related to the physicochemical properties of the reactants, but also to the packaging quality and packaging materials. The STAD is calculated by linear regression of Eq. (2).

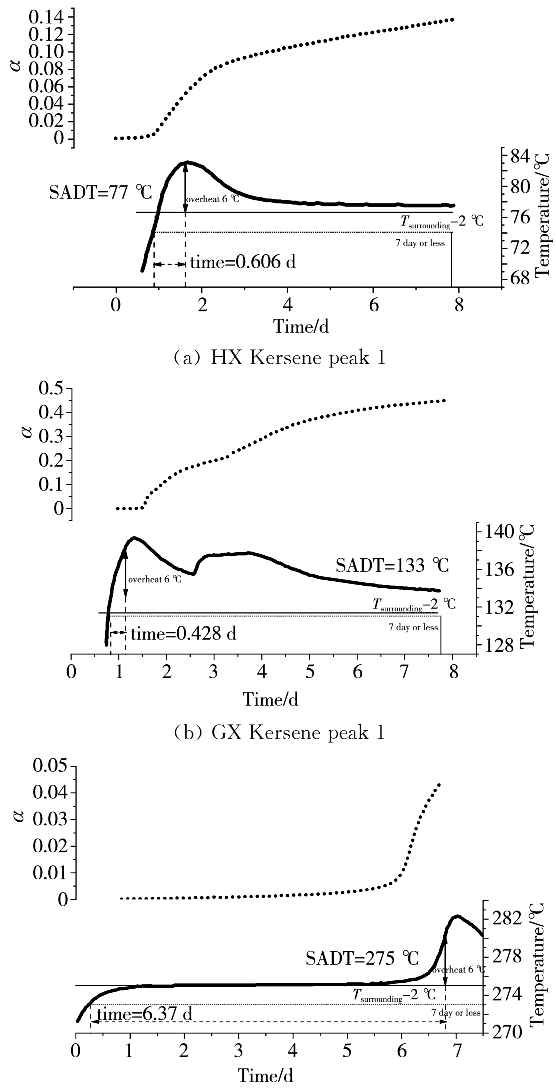
$$T_{0/e/p} = T_{00/e0/p0+} + b\beta_i + c\beta_i^2 + d\beta_i^3, \qquad (2)$$

where b, c, d are coefficients; β_i is the heating rate, K · min^{-1}. T_0 is the initial decomposition temperature, K; T_e is the temperature corresponding to the intersection of the tangent line at the maximum slope of the DSC curve and the epitaxial baseline, K; T_p is the peak temperature, K. At the rate of temperature rise tends to 0, above mentioned factors are brought into Eq. (2) to obtain the corresponding as T_{00}, T_{e0} (SADT) and T_{p0}.

Using AKTS thermal safety software, SADT simulations are performed for each of the three kerosene types with different exothermic peaks. The ambient temperature for sample storage is −2 ℃, and the packaging mass is 50 kg. The results are shown in Fig. 9.

It can be obtained that the self-accelerating decomposition temperature of HX kerosene is 77 ℃, and the sample temperature at 0.606 d is 6 ℃ higher than the ambient temperature at this time. The temperature of the self-accelerating decomposition of the first exothermic peak of GX kerosene is 133 ℃, and the temperature of the sample at 0.428 d is 6 ℃

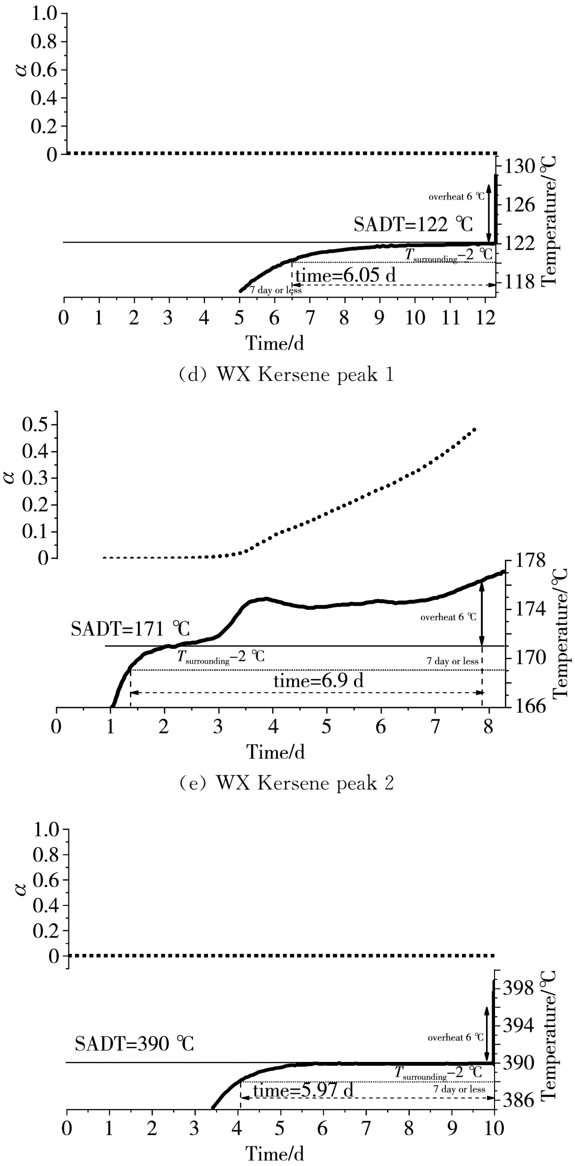
higher than the ambient temperature. The temperature of the second exothermic peak of GX kerosene is 275 ℃, the sample temperature at 6.37 d is 6 ℃ higher than the ambient temperature at this time. The SADT of the first exothermic peak of WX kerosene is 122 ℃, and the sample temperature at 6.05 d is 6 ℃ higher than the ambient temperature at this time. The SADT of the second exothermic peak is 171 ℃, and the sample temperature at 6.9 d is 6 ℃ higher than the ambient temperature at this time. The third exothermic peak SADT is 390 ℃, and the sample temperature at 5.97 d is 6 ℃ higher than the ambient temperature at this time. Among the three kinds of kerosene under the same conditions, HX kerosene has the lowest self-accelerating decomposition temperature and the lowest safety. Therefore, in the practical application of kerosene, a good ventilation environment should be ensured to reduce heat accumulation to ensure the safety of production, transportation and storage.



(a) HX Kersene peak 1

(b) GX Kersene peak 1

(c) GX Kersene peak 2



(d) WX Kersene peak 1

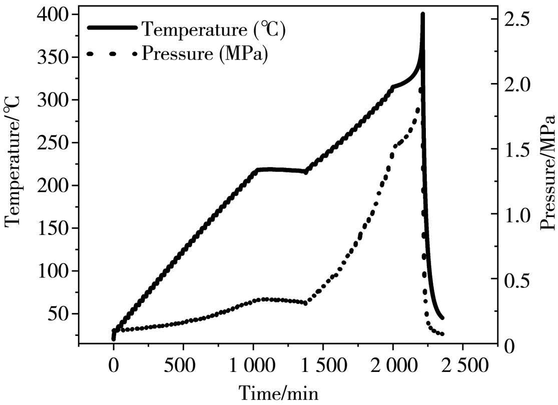
(e) WX Kersene peak 2

(f) WX Kersene peak 3

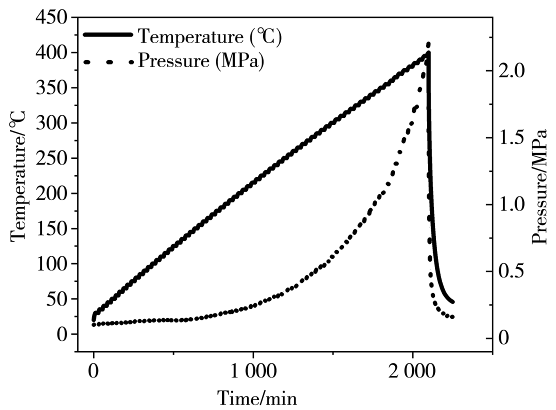
Fig. 9 SADT prediction results of three kinds of kerosene

2.3 ARC results of coal-based aerospace kerosene

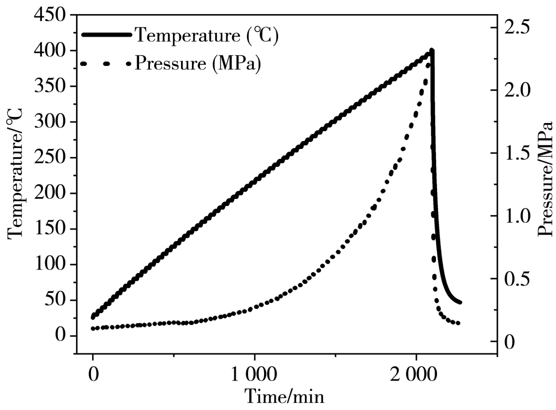
The ARC test is used to evaluate the safety of chemicals by maintaining the sample in an adiabatic environment and measuring data such as time, temperature and pressure during the exothermic reaction. ARC test results of three kinds of kerosene are summarized in Fig. 10. The experimental results show that the exothermic heat of HX kerosene and WX keroseneare not detected during the experimental process, and the pressure rise is relatively moderate. It is observed from Fig. 10(a) that when the temperature reaches 315 ℃, the temperature and pressure of the GX kerosene sample suddenly increase with a large amplitude. It shows that GX kerosene has a significant exotherm during the test (the initial decomposition temperature is 315 ℃). Consequently, the thermal stability of GX kerosene under adiabatic conditions is low, and the possibility of accidents is high. This is due to the addition of a small amount of active additives to GX kerosene, which makes it more sensitive to thermal effects.



(a) GX Kerosene



(b) HX Kerosene

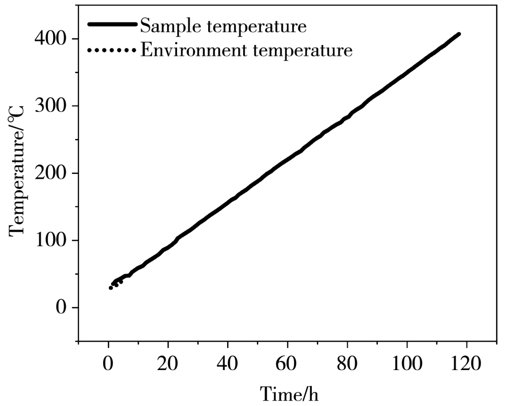


(c) WX Kerosene

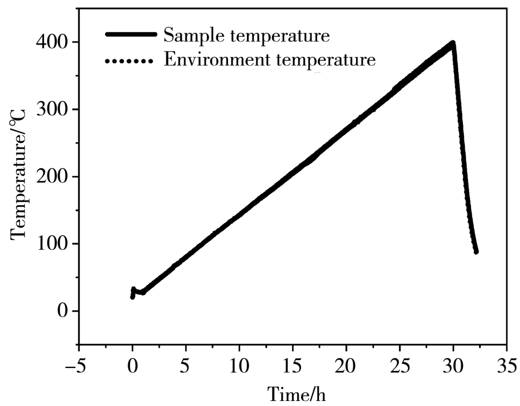
Fig. 10 Temperature and pressure-time curves of ARC test for three kinds of kerosene

2.4 High-temperature stability of coal-based aerospace kerosene

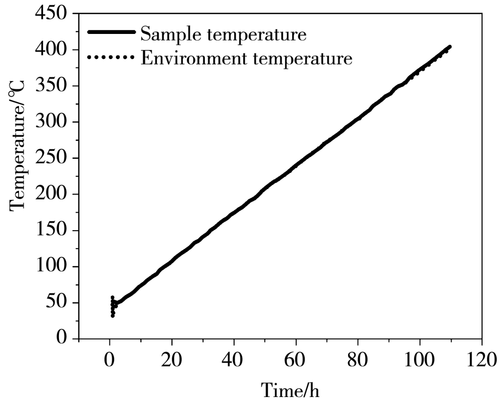
The experimental results of high-temperature stability of the three kinds of kerosene are shown in Fig. 11. It can be observed that GX kerosene, HX kerosene and WX kerosene have no temperature abrupt change and no reaction during the test, indicating that these three kerosene have good stability under high temperature conditions.



(a) GX Kerosene



(b) HX Kerosene



(c) WX Kerosene

Fig. 11 Sample temperature curve

3 Conclusions

1) GX kerosene has the lowest flash point, with an open cup flash point of 43 ℃ and a closed cup flash point of 37 ℃. The lower explosion limits of GX kerosene, HX kerosene and WX kerosene steam are 1.81%, 3.74% and 3.93%, respectively. Among them, GX kerosene steam has the lowest lower

explosion limit. Thus GX kerosene is more sensitive than the other two kinds of kerosene, and the risk of transportation and storage is higher.

2) The high temperature stability of the three kinds of kerosene meets the requirements. The DSC test shows that the decomposition intensity of three kinds of kerosene is different, with HX kerosene decomposing most vigorously while GX kerosene decomposed more gently. The initial decomposition temperature of HX kerosene is the lowest, and the heat release of GX kerosene is the highest. According to the thermal analysis kinetics, the apparent activation energy and T_{D24} of HX kerosene are the lowest among the three kinds of kerosene, and its thermal safety is the lowest. ARC test shows that only GX kerosene has obvious heat release during the testing process, indicating that its thermal stability is the lowest among the three kinds of kerosene under adiabatic conditions.

3) During the actual production, use, storage and transportation of kerosene, fireworks should be strictly prohibited, away from flammable materials, and should be stored in qualified and safe containers. The container of kerosene should be tightly covered at all times to avoid combustible kerosene vapor from being emitted. During storage of kerosene, avoid placing it in an adiabatic environment or bulk accumulation. Kerosene should be stored at room temperature in a ventilated and dry place to ensure heat dissipation.

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煤基航天煤油安全特性分析

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摘　要： 本文研究了GX煤油、HX煤油、WX煤油3种典型煤油的危险性和热安全特性。首先，利用自行设计的爆炸极限测量系统，确定了3种煤油蒸汽的爆炸下限。然后，使用差示扫描量热仪(DSC)对煤油进行线性加热实验，分析煤油的热分解特性。采用动力学方法计算并比较了3种煤油的热解动力学参数。实验结果表明：GX煤油的闪点及爆炸下限相对较低。DSC测试表明，HX煤油的最低初始分解温度为116.5 ℃。由热解动力学计算可知，HX煤油的 T_{D24} 与表观活化能较小。由ARC试验得到，在绝热条件下GX煤油的热稳定性最差。3种煤油的高温稳定性均可达到要求。综合来看，GX煤油的危险性最高，HX煤油的热安全性最低，故在煤油的储运过程中要防止热量的累积。此研究提供了煤基航天煤油基础的安全特性数据，为发动机可靠性增长与性能提升提供了技术支撑。

关键词： 航天煤油；危险性；热解动力学；热安全性

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