

THERMAL HAZARD EVALUATION OF COMPLEX REACTIVE SUBSTANCE USING CALORIMETERS AND DEWAR VESSEL

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(Received June 17, 2003; in revised form February 13, 2004)

Abstract

In this paper, several small-scale screening test methods were discussed on evaluating the thermal hazard of reactive substances. Generally the sensitivities of DSC and ARC are not high enough to evaluate the thermal hazards for all reactive substance, especially, for those of complex reactions containing a phase and/or chemical reaction mechanism change in the lower temperature range. Using the C80, however, the reaction can easily be detected in the lower temperature range due to its high sensitivity. Therefore, the C80 gives generally more accurate results than DSC and ARC.

Data from C80 and Dewar vessel were compared and it indicates that the Dewar vessel has also high enough sensitivity to evaluate the thermal hazard and determine the heat flux in lower temperature range of reactive substances.

Keywords: calorimeter, Dewar vessel, reactive substance, thermal hazard evaluation

Introduction

Chemical reaction hazards are associated with thermal runaway, which occurs when the heat generated by a reaction exceeds the heat transferred into the surroundings. The surplus heat increases the temperature of the reaction mass, which causes the reaction rate to increase and in turn accelerates the rate of heat production. Thermal runaway occurs because, as the temperature rises, the rate of heat loss to the surroundings increases linearly with temperature, but the rate of reaction, as well as the rate of heat generation increases exponentially. As a result, heat accumulation may start slowly but then accelerate, until eventually leading to a runaway reaction.

In order to evaluate the thermal hazards of reactive substances, the knowledge on their reactivity and their heat release are necessary. It is clearly not safe to test unknown reactants or compounds in a full-size reactor, as a vigorous exotherm may

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overcome the protection systems provided. Various theoretical techniques and small-scale tests have therefore been devised to provide data on the likelihood and severity of a runaway reaction. Several small-scale screening tests are characterized by the small sample sizes (0.01–10 g) and the speed with which they can be performed [1–9]. They are differential scanning calorimeter (DSC) and various forms of differential thermal analysis (DTA), the accelerating rate calorimeter (ARC), and the heat flux calorimeter (C80) and so on. Based on such small-scale screening tests, the thermal hazard of full-size plant can be simulated. However, due to their different sensitivity and measurable temperature region such small-scale screening tests are not always valid for the thermal hazard evaluation of all kinds of reactive substances.

In this paper, the small-scale screening test methods (such as DSC method, ARC method, C80 method) for evaluating the thermal hazards of reactive substances were discussed. In the experiment, a complex reactive substance, which was produced by mixing liquid waste, containing NaNO_3 , NaNO_2 , Na_2CO_3 , NaH_2PO_4 and other salts, with high temperature asphalt in an extruder was tested. Such a mixture caused a fire and explosion accident at the Bituminization Demonstration Facility in the Tokai Works of the Power Reactor and Nuclear Fuel Development Corporation in Japan on 11 March 1997 [10, 11]. What happened was that a 220 L steel drum was filled with the asphalt–salts mixture at about 180°C and about 20 h later a fire broke out from the drum. It was thought that the oxidation–reduction reaction between the asphalt and a salt in the mixture during a cooling period initiated at the filling temperature, and the heat release accumulated in the drum, eventually led to a run-away reaction.

Sensitivity of calorimeters

Figure 1 shows the sensitivity and measurable temperature range of several calorimeters. It can be seen that, although the calorimeters such as thermal activity monitor (TAM), micro DSC and micro heat flux calorimeter (MS80) have very high sensitivity, their measurable temperature range is not wide enough. On the other hand, the

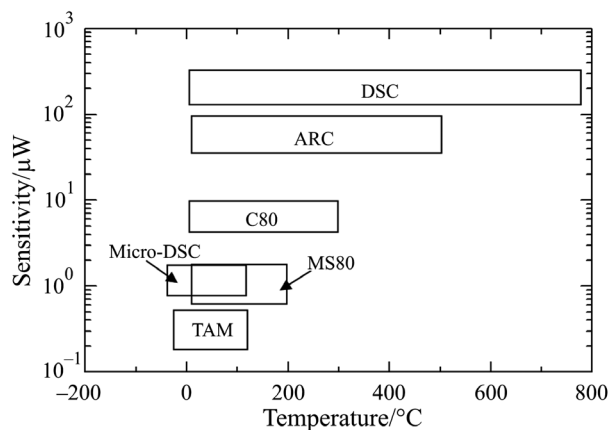


Fig. 1 Sensitivity and measurable temperature range of several calorimeters

calorimeters such as DSC and ARC have very wide measurable temperature range, however, due to their low sensitivity, it would be difficult for them to measure the heat generation and reactivity for those substances which have a faint heat generation or to accurately measure the initial range of a reaction which normally is below the detection limitation of the apparatus but can never be negligible. If such a calorimeter is used to evaluate the thermal hazards of the reactive substance, the reaction data at high temperature has to be extrapolated into lower temperature range under the assumption of a zero order reaction [1–4].

Small-scale thermal hazard evaluation methods

In this study, a complex mixture, asphalt–salts mixture which was prepared by mixing liquid waste, containing NaNO_3 , NaNO_2 , Na_2CO_3 , NaH_2PO_4 and other salts, with high temperature asphalt in laboratory was used to discuss the thermal hazard evaluation method by using thermal calorimeters (DSC, ARC, C80) and Dewar vessel. The results obtained by using different measurement method were compared.

C80 experiment

C80 is a heat flux calorimeter manufactured by Setaram in France. It has the merit of high sensitivity, with several μW at least and many functions and a quite wide testing temperature range from room temperature to 300°C . By using different types of experiment vessel with sample mass up to about 10 g and different function, a great number of measurements can be made with C80, such as heat capacity determination of substances; heat generation by a change of state, mixing or a chemical reaction; determination of reactivity and kinetic parameters of reactive substance; hazards evaluation of reactive substance and so on [4–7].

A low heating rate experiment is appropriate to examine reactive heat behaviour at lower temperature. Therefore, in this study, a very slow temperature rise rate ($0.01^\circ\text{C min}^{-1}$) experiment and isothermal experiment were used to measure the reactivity and heat generation of asphalt–salts mixture. Figure 2 shows the heat flux of the asphalt–salts mixture (sample mass: 0.500 g, temperature rise rate: $0.01^\circ\text{C min}^{-1}$) measured by C80. The heat flux increases very slowly and gradually with temperature increase in the range 160 – 195°C , keeps almost constant in the range 195 – 245°C , and increases sharply above 245°C . Therefore, the reaction of salts with asphalt can be divided into three stages corresponding to these three temperature ranges. In the first stage, liquid asphalt could contact directly with oxidizing salts so the rate-determining step may be chemical reaction, as indicated by the dependence of rate upon temperature. As this reaction proceeds, it can be assumed that a layer of the reaction product forms on the surface of the salt particles. Thus in the second stage, when the layer of reaction product becomes thicker, the rate becomes diffusion controlled and almost independent of temperature. In the third stage, when the temperature exceeds the melting point of oxidizing salts, the reaction mechanism changes

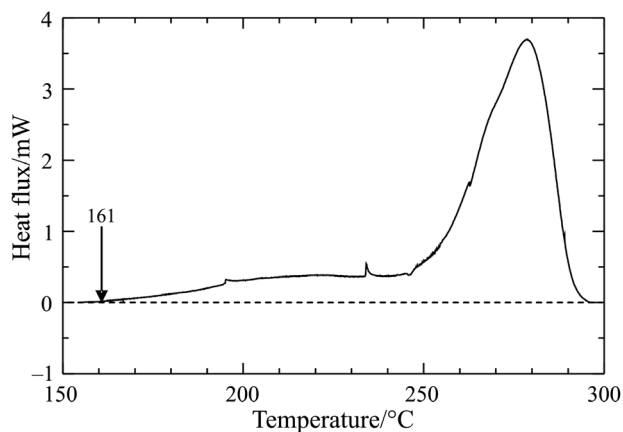


Fig. 2 Heat flux curve of the asphalt-salts mixture measured by C80, sample mass: 0.500 g, temperature rise rate: $0.01^{\circ}\text{C min}^{-1}$

from a solid-liquid interface reaction into a liquid-liquid reaction and the heat flux increases exponentially with temperature.

Figure 3 shows the isothermal experiment results of the asphalt-salts mixture (sample mass 1.000 g) measured by the heat flux calorimeter of C80 with high sensitivity (less than $10 \mu\text{W}$). It is seen for both results at temperatures 170 and 180°C that heat flows decrease quickly in the first 500 min and then decrease slowly from 500 to 2000 min. When the time exceeds 2000 min, the heat flows almost keep constant. It is because at first, the liquid asphalt could contact directly with oxidizing salts, the reaction rate must be faster, and it decreases quickly due to the consumption of asphalt and salts at the contact area. As this reaction proceeds, it can be imagined that a layer of the reaction product forms on the surface of the salt particles, the asphalt or

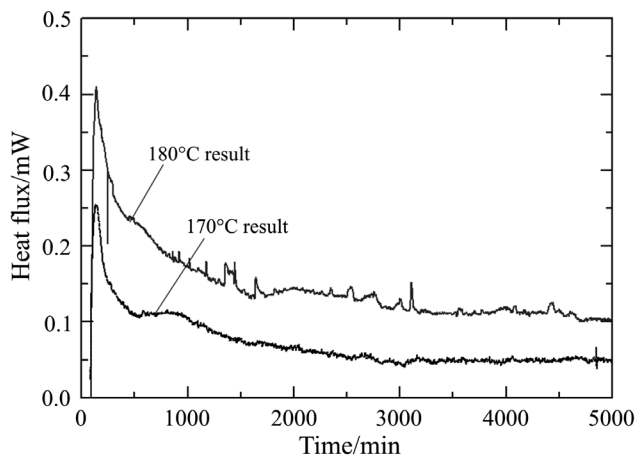


Fig. 3 Isothermal experiment results of the asphalt-salts mixture, sample mass 1.000 g

salt has to cross the product layer to react with each other. Therefore, the heat flow almost keeps constant when the time exceeds 2000 min due to the diffusion controlled of reactive substance.

DSC experiment

DSC is an effective tool for the study on the thermal stability, heat generation by a change of state, mixing or a chemical reaction, kinetic parameters of reaction and decomposition of reactive substance and so on [9, 12, 13]. In a typical DSC apparatus a small amount of sample (1–20 mg) is placed in a metal capsule and heated at a constant rate (1–10 K min⁻¹) in the range from room temperature to 800°C. It is suitable as a fast screening test to measure the reactivity and heat generation of most reactive substance in safety.

Figure 4 shows the relationship between heat flow and temperature of the same asphalt–salts mixture sample measured by DSC (sample mass: 0.01495 g; temperature rise rate: 2.5°C min⁻¹; atmosphere: N₂). The measured result shows that the heat generation is only detected when the temperature exceeds 290°C, much higher than that of C80. The first two stages of C80 result do not appear in the record heat curve. This would be caused by the low sensitivity of DSC and fast temperature rise rate of 2.5°C min⁻¹. However, even if using the minimum temperature rise rate of 1°C min⁻¹, the measured result almost has no difference with that one of 2.5°C min⁻¹. On the other hand, the sample mass used for DSC experiment is too small, that also is a significant limitation of DSC.

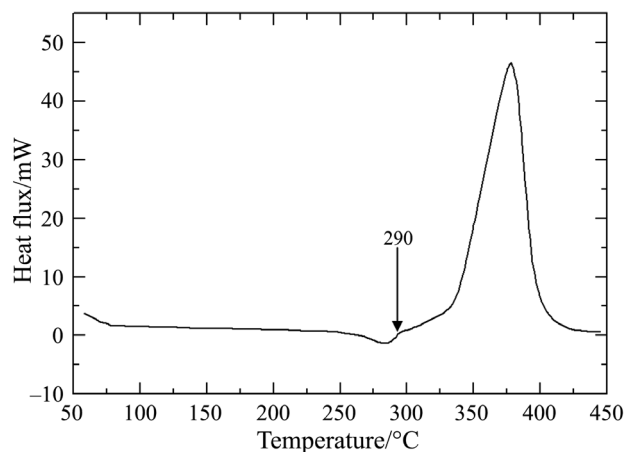


Fig. 4 Heat flux curve of the asphalt–salts mixture measured by DSC, sample mass: 14.95 mg, temperature rise rate: 2.5°C min⁻¹

ARC experiment

ARC (adiabatic rate calorimeter) is an effective tool for hazards evaluation of reactive substance [1–3, 9]. It uses a titanium or stainless steel sample holder (bomb) of up

to 10 g sample mass, fitted with temperature and pressure transducers. The bomb is placed inside a nickel-plated copper jacket, and the whole is enclosed in a steel safety casing. The instrument normally operates using the heat-wait-search technique. It increases the sample temperature in small steps, pausing after each step to see if it can detect a temperature rise greater than 0.02 K min^{-1} , indicating self-heating. Once the sample starts to self-heat, the instrument increases the jacket temperature to follow the temperature rise of the sample, meanwhile recording the elapsed time, temperature and pressure. The data measured by the ARC such as: self-heating rate vs. temperature; time to maximum self-heating rate; pressure vs. temperature and so on, can be applied to the evaluation of thermal and pressure hazards.

Figure 5 shows the self-heating rate vs. temperature plot of the same sample (sample mass is 1.10 g, $\phi=2.45$). It is seen that, the heat release can only be detected when the temperature exceeds 271°C . This result is similar to that of DSC. The failure to obtain the reaction and heat generation in the lower temperature range also lies in its low detection sensitivity and high thermal inertia (ϕ value) of 2.45.

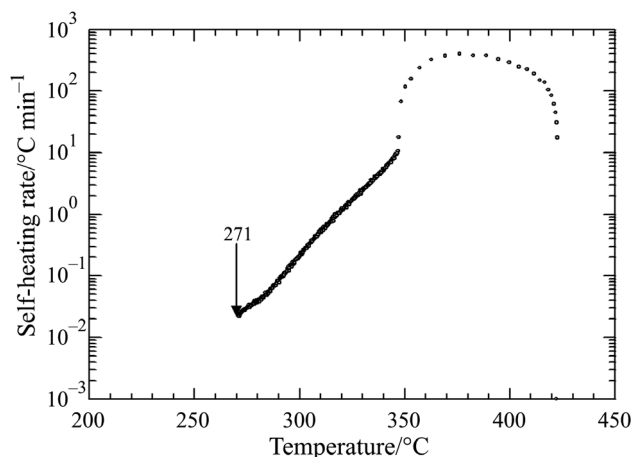


Fig. 5 The relationship between self-heating rate and temperature of the asphalt-salts mixture measured by ARC, sample mass: 1.10 g, $\phi=2.45$

Even though the method by extrapolating the reaction data into the lower temperature range under the assumption of a zero order reaction to evaluate reaction data at lower temperature range. The extrapolating method is only suitable for reactions, which follow a simple reaction scheme without phase change or chemical reaction mechanism change at the lower temperature range. That is to say, when a physical phenomenon such as melting or evaporating occurs and/or a chemical reaction mechanism changes occur at the lower temperature range, the reaction-extrapolating method must lead the evaluated result into error. In the case of the asphalt-salts mixture, there is not only phase change, but also chemical reaction mechanism change in the lower temperature (under 245°C) [10].

It is clear that the onset temperatures of the asphalt–salts mixture measured by DSC and ARC are much higher than its real runaway reaction temperature of about 180°C, for such a case, the use of the thermal hazards evaluation results obtained by DSC and ARC must be very dangerous. In other words, the DSC and ARC are not suitable for thermal hazard evaluation of those reactive substances, which are very complex reaction containing phase change (melting or evaporating) and/or a chemical reaction mechanism changes in the lower temperature.

Comparison of experimental results of small-scale test and Dewar test

Dewar experiment

Dewar calorimeter, which uses a vacuum-jacketed flask to measure thermal effects, is one of the simplest calorimetric methods. A Dewar experiment, one of the most useful techniques in assessment of chemical reaction hazards, is herein developed to carry out such a strictly adiabatic self-heating test under lowest amount of filling sample [14]. Figure 6 shows the construction of Dewar experimental apparatus. The Dewar was placed in an oven, the temperature of which can be controlled from room temperature to 300°C. The Dewar was equipped with three thermocouples, the diameter of which was 1 mm in a type of sheath, to monitor the temperatures at different sites like the center, bottom and upper surface of the sample. All the thermocouples including one measuring the ambient were connected to a recorder and a computer to collect raw data. In the experiments, two kinds of Dewar vessel were used. 500 mL cylinder-shaped Dewar was used to do a temperature controlling experiment and 1000 mL spherical Dewar was used to do an isothermal experiment. For the former experiment, the atmospheric temperature in the chamber of the oven was manually controlled so that it followed the Dewar internal sample's temperature by the increment of 1°C.

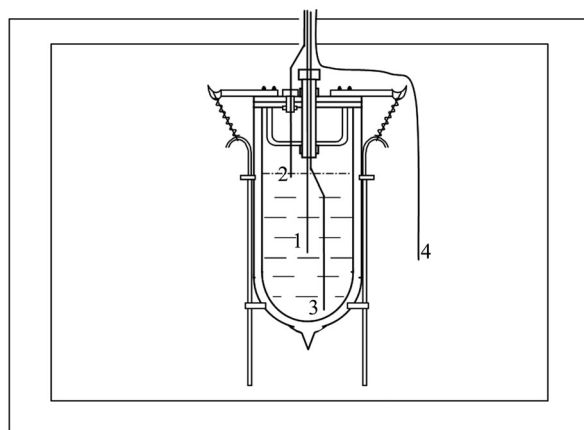


Fig. 6 The construction of Dewar experiment system (1, 2, 3, 4 – thermocouples)

Figure 7 shows temperatures vs. time curves of the asphalt–salts mixture inside 500 mL Dewar under initial 190°C, in which T_1 , T_2 , T_3 and T_4 refer to the temperatures of the center, the upper surface, the bottom of the sample in Dewar and the ambient, respectively. When the sample's temperature inside went by 1°C up to the ambient since its self-heating, the ambient temperature was changed ladderlike by the increment of 1, until above 265°C when the inside temperature rose quickly, the manually controlled ambient followed no longer i.e., runaway reaction. Finally the sample's temperature went beyond 290°C, and the sample burned violently. This initial temperature 190°C is much close to that temperature of 180°C when an accident happened.

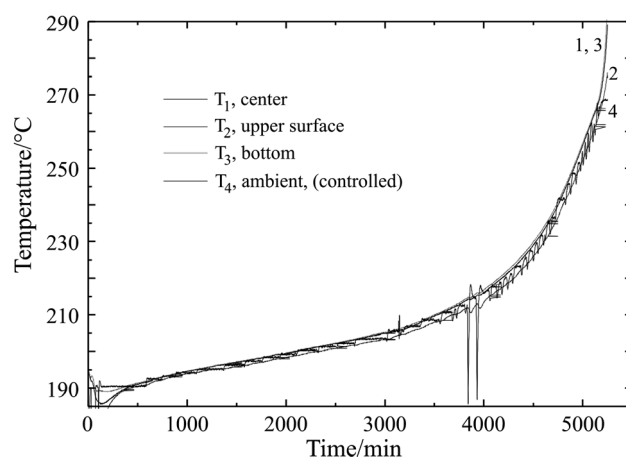


Fig. 7 Temperatures vs. curves of the asphalt–salts mixture in 500 mL Dewar under initial 190°C

Figure 8 shows the isothermal experiment results of the relationships between sample temperatures and time in presence of the ambient temperature at 170°C. It can be seen that the sample temperatures increase quite quick initially, reached the maximums, and then keep almost constant. It means that even if at the low temperature 170°C, the sample has large enough heat generation to heat itself. If the sample mass is huge, a runaway reaction must be happened around this temperature.

According to the Semenov model [15], the uniform temperature rise rate in a reaction system is established by the difference between the rate of heat generation from the system and the rate of heat transfer to the environment as the following equation:

$$C_p M_0 \frac{dT}{dt} = M_0 \frac{dH}{dt} - US(T - T_0)$$

where C_p is specific heat (J g^{-1}); dH/dt is heat flow ($\text{J s}^{-1} \text{g}^{-1}$); M_0 is initial mass of reactant (g); S is contact area between Dewar and surroundings (m^2); T and T_0 are sample temperature and ambient temperature (K), respectively; U is overall heat transfer coefficient of Dewar ($\text{J m}^{-2} \text{K}^{-1} \text{s}^{-1}$).

Comparison of experimental results

On the basis of the above equation and the measured data of Fig. 8, heat flux at 170°C can be calculated, as shown in Fig. 9. The isothermal result (temperature: 170°C, sample mass: 1.00 g) measured by C80 is shown in the same figure. It is evident that the isothermal results of heat flow obtained from Dewar experiment and C80 calorimeter have the similar tendency. It means that the Dewar has also high enough sensitivity to get accurate information of heat flux in the lower temperature range.

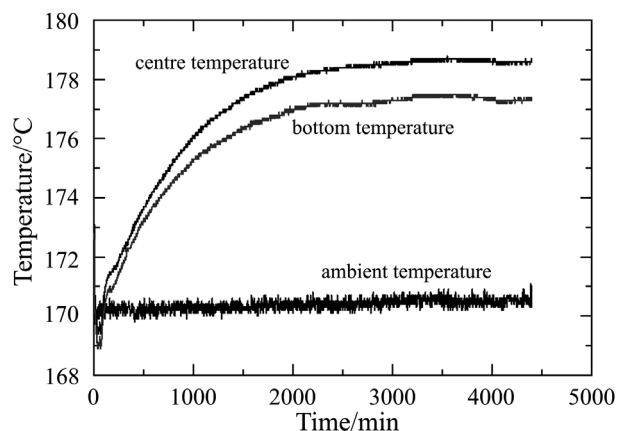


Fig. 8 The relationships between sample temperatures and time of the asphalt-salts mixture in 1 L Dewar at 170°C

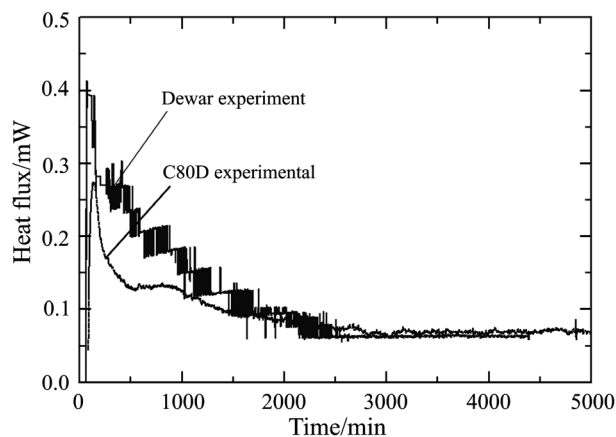


Fig. 9 Isothermal results of the asphalt-salts mixture at 170°C obtained from C80 and Dewar vessel, sample mass: 1.00 g

The onset temperature and calculated self-accelerating decomposition temperature (SADT) of the asphalt-salts mixture obtained by different method are shown in

Table 1. It is clear that the onset temperature and SADT obtained by C80 and Dewar vessel are lower than the accident temperature of 180°C; the SADT of 173°C calculated by C80 data is in good agreement with the SADT of 170°C determined by a direct measurement test of Dewar, this is because the reaction can be usually detected in the vicinity of the SADT due to the high sensitivity of C80. However, on the other hand, the SADT calculated by ARC and DSC data are much higher than the Dewar experiment result, because the reaction cannot be detected in the vicinity of the SADT due to the lower sensitivity of ARC and DSC, the reaction data have to be extrapolated into lower temperature range of the SADT under the assumption of a same reaction mechanism. In other words, when a physical phenomenon such as melting or evaporating occurs and/or changes in the chemical reaction mechanism occurs between the onset temperature and the SADT, the reaction-extrapolating method must lead the evaluated SADT into error. The sample used in this study has not only a phase change (salts melting) but also a chemical reaction mechanism change below the onset temperature of ARC and DSC [9], therefore, the ARC and DSC methods are not suitable for evaluating the thermal hazard of such reactive complex substances.

Table 1 Onset temperature and SADT of asphalt–salts mixture obtained by different method

Method	Onset temperature/°C	SADT/°C	
		calculated	experiment
C80	161	173	
ARC	271	245	
DSC	290	256	
Dewar experiment	160		170

Conclusions

In this paper, the uses of calorimeters and Dewar vessel for evaluating the thermal hazards of reactive substance were discussed, and following conclusions were drawn.

- Generally the sensitivity of DSC and ARC are not enough to get accurate information of reaction and heat generation for all of the reactive substance, especially, for those reactive substances, which have very complex reactions containing a phase and/or chemical reaction mechanism change in the lower temperature range, the faint heat exchange may not be detected by these instruments and hence the accurate extrapolation for SADT can not be obtained. For the sample of asphalt–salts mixture used in this study, the error of calculated SADTs by ARC and DSC are larger than 75°C.
- With the C80, the reaction can be usually detected in the lower temperature range due to its high sensitivity. Therefore, the C80 gives generally more accurate results than DSC and ARC.

- The Dewar vessel has also high enough sensitivity (as high as C80) to evaluate the thermal hazard and to determine the reaction characteristics in lower temperature range of reactive substances. It means that it is an alternative to get very accurate information of heat flux without those expensive thermal calorimeters in practice.

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This study was supported by the '100 Talents Project' of Chinese Academy of Sciences and China NKBRFSF project, No. 2001CB409600.

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