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Comparative analysis of the methods for SADT determination

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Abstract

The self-accelerating decomposition temperature (SADT) is an important parameter that characterizes thermal safety at transport of self-reactive substances. A great many articles were published focusing on various methodological aspects of SADT determination. Nevertheless there remain several serious problems that require further analysis and solution. Some of them are considered in the paper.

Firstly four methods suggested by the United Nations "Recommendations on the Transport of Dangerous Goods" (TDG) are surveyed in order to reveal their features and limitations.

The inconsistency between two definitions of SADT is discussed afterwards. One definition is the basis for the US SADT test and the heat accumulation storage test (Dewar test), another one is used when the Adiabatic storage test or the Isothermal storage test are applied. It is shown that this inconsistency may result in getting different and, in some cases, unsafe estimates of SADT.

Then the applicability of the Dewar test for determination of SADT for solids is considered. It is shown that this test can be restrictedly applied for solids provided that the appropriate scale-up procedure is available. The advanced method based on the theory of regular cooling mode is proposed, which ensures more reliable results of the Dewar test application.

The last part of the paper demonstrates how the kinetics-based simulation method helps in evaluation of SADT in those complex but practical cases (in particular, stack of packagings) when neither of the methods recommended by TDG can be used.

Keywords: SADT; Thermal explosion; Reactive chemicals; Mathematical simulation

1. Introduction

The self-accelerating decomposition temperature (the SADT) is an important parameter that characterizes thermal hazard under transport conditions of condensed self-reactive substances. The SADT has been introduced into the international practice by the United Nations "Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria" (TDG) [1]. The Globally Harmonized System (GHS) [2] had inherited the SADT as a classification criterion for self-reactive substances. According to TDG the SADT is defined as "the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging as used in transport". Important feature of the SADT is that it is not an intrinsic property of a substance but "... a measure of the combined effect of the ambient temperature, decomposition kinetics, packaging size and the heat transfer properties of the substance and its packaging" [1].

If the SADT $\leq 50\,^{\circ}C$ for organic peroxides and $\leq 55\,^{\circ}C$ for self-reactive substances, the following control and emergency temperatures are set for a packaging (Table 1).

The Manual recommends four tests for determining the SADT:

1. The United States SADT test (US SADT test) H1.
2. Adiabatic storage test (AST) H2.
3. Isothermal storage test (IST) H3.
4. Heat accumulation storage test (Dewar test) H4.

The H1 test foresees the experimental determination of the SADT for a commercial packaging. The H4 test is also based on experimental determination of the SADT for a small Dewar vessel, which is supposed to be representative for a commercial packaging provided that the special scale-up procedure is used.

The H2 and H3 tests are based on the use of adiabatic and isothermal calorimetric technique respectively with the following estimation of the SADT.

The US SADT test is the only method that gives the direct and, hence, the most reliable answer. Nevertheless it is used rather

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Nomenclature

a	thermal diffusivity ($a = \lambda/c_p/\rho$, m^2/s)
c_p	specific heat of a product (J/kg/K)
dQ/dt	specific rate of heat generation due to a reaction (W/kg)
E	activation energy (kJ/mol)
h	height of a barrel (m)
$[k_0]$	preexponential factor (s^{-1})
m_p	mass of a product (kg)
Q^{∞}	heat effect of a reaction (J/kg)
r	radius of a barrel (m)
R	universal gas constant ($R = 8.31$ J/mol/K)
S	surface of heat exchange (m^2)
T	temperature (K)
T_{CR}	critical temperature of thermal explosion (K)
T_e	ambient temperature (K)
$[T_0]$	initial temperature of a product (K)
U	heat transfer coefficient ($W/m^2/K$)
$(US)/m$	specific heat loss (W/kg/K)
V	volume of a vessel or a package (m^3)
z	autocatalytic constant

Greek letters

α	degree of conversion
$[\Delta T_6]$	the characteristic 6 °C overheat in the middle of a package ($\Delta T_6 = 6$ °C)
λ	thermal conductivity coefficient (W/m/K)
μ_i	roots of the characteristic equation
ρ	product density (kg/m^3)
ω	cooling tempo (s^{-1})

rarely because of its expensiveness. Moreover this test can be applied only for packagings of up to 220 L so that large tanks or intermediate bulk containers (IBSs) turn out to be out of the scope of this test. The H2–H4 tests are very attractive because they are based on the lab-scale experiments, do not involve such a large amount of reactive product and therefore are less expensive and dangerous. At the same time all these tests have essential limitations that should be taken into account when selecting one or another test.

Detailed analysis of problems related to the SADT determination methods have been presented by Fisher [3], numerous more recent papers are focused on correctness of some particular methods (see, for instance [4–10]). This paper continues discussion of certain important aspects of the SADT determination methods. The consideration is illustrated by the abstract simulated examples that are capable of conveying the ideas without superfluous details. The numerical simulations were implemented by using the Fork and ThremEx program packages developed by CISP [11].

2. Overview of the methods for SADT determination

2.1. The United States SADT test H1

The US SADT test H1 (and the Dewar test H4) is based on the following definition of the SADT:

$$\begin{aligned}&SADT\ is\ the\ lowest\ environment\ (oven)\ temperature\ at\ which\\&\quad overheat\ in\ the\ middle\ of\ the\ specific\ commercial\\&\quad packaging\ exceeds\ 6\,^{\circ}C\ after\ a\ lapse\ of\ the\ period\\&\quad of\ 7\ days\ (168\ h)\ or\ less\end{aligned} \qquad (D1)$$

This period is measured from the time when the packaging center temperature reaches 2 °C below the oven temperature (Fig. 1a).

The US SADT test represents the series of full-scale experiments that are carried out with the specific commercial packagings of a product. The packaging is inserted in the test chamber (oven) and is maintained at a constant oven temperature. The temperature in the center of the packaging is monitored. Every experiment of the series is implemented with the new packaging. The step of the oven temperature variation is 5 °C.

According to the thermal explosion theory the essential attribute of an explosion is the critical temperature T_{CR} which, for a packaging of given size, delimits the explosive and non-explosive domains of reaction proceeding. What is the relation between the SADT based on the characteristic overheat ΔT_6, which is used as the criterion, and T_{CR}? To answer this question we considered two cases when the simple first-order reaction and the autocatalytic reaction occur in a product ($\rho = 1000\ kg/m^3$; $c_p = 2000$ J/kg/K). In both the cases an explosion in the barrel of 0.6 m height and 0.2 m radius ($S = 1\ m^2$, $V = 75$ L) had been simulated assuming that temperature distribution in the barrel is uniform (model of a well stirred tank, hereafter referred to as the lumped system). This model is suitable for low-viscous liquids. The initial temperature T_0 is 20 °C, boundary conditions of the 3rd kind with heat transfer coefficient $U = 4.7\ W/m^2/K$ were specified on all the external surfaces of the barrel. Mass of a product was 75 kg.

Table 1
Derivation of control and emergency temperatures

Receptacle	Group	SADT	Control t-re	Emergency t-re
	1	20 °C or less	20 °C below SADT	10 °C below SADT
Single packagings and IBSs	2	Over 20–35 °C	15 °C below SADT	10 °C below SADT
	3	Over 35 °C	10 °C below SADT	5 °C below SADT
Portable tanks	4	<50 °C	10 °C below SADT	5 °C below SADT