Thermochimica Acta xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal decomposition of AIBN: Part D: Verification of simulation method for SADT determination based on AIBN benchmark

Arcady A. Kossoy*, Vasily M. Belokhvostov, Elena Yu. Koludarova

ChemInform St. Petersburg (CISP) Ltd., 193232 PO box 25, Saint Petersburg, Russia

ARTICLE INFO

Article history:
Received 16 March 2015
Received in revised form 30 May 2015
Accepted 8 June 2015
Available online xxx

Keywords:
Calorimetry
Reaction kinetics
Thermal explosion
Numerical simulation
Software
SADT

ABSTRACT

The advantages of simulation-based method for the SADT determination are widely recognized. Nevertheless, active introduction of this method in practice requires careful verification. The project proposed by the Federal Institute for Materials Research and Testing, BAM, pursued this very object. Decomposition of 2,2′-azobis(isobutyronitrile), AIBN, has been studied by DSC in isothermal mode and series of large-scale experiments (H1 and H4 tests) have been implemented. All these data were available for processing, simulation, and comparison with the experimentally determined SADT.

This paper represents the results achieved by "ChemInform" Ltd. Firstly the formal kinetic model has been created that provided appropriate fit of calorimetric data. Then this model was used for simulation of the conditions of H1 and H4 experiments. The results demonstrate good correspondence with experimental data.

The materials presented show the potential of the simulation-based method as very useful addition to the methods recommended by international regulations.

The CISP TSS software was used for implementing all the steps of the study.

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 and organic peroxides. The SADT has been introduced by the UN "Recommendations on the Transport of Dangerous Goods", TDG [1], then inherited by the Globally Harmonized System, GHS, [2] as a classification criterion for two classes—self-reactive substances and organic peroxides. Other international and national regulations (e.g., REACH [3], ADR [4] and many others) also inherited the SADT and the methods for its determination.

The TDG Manual recommends four tests H.1–H.4 for experimental determination of the SADT. The United States SADT test H.1 is the only one that foresees the experimental determination of the SADT for a commercial packaging thus giving the direct and most reliable answer. Nevertheless, it is rarely used 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 (IBCs) turn out to be out of the scope of this test.

The H.2 and H.3 tests are quite popular as they are based on the lab-scale experiments but they require the appropriate scale-up procedures and have essential limitations.

The H.4 heat accumulation test is regarded as very reliable method. Similar to the H.1 test it is based on experimental determination of the SADT for a small DEWAR flask (typically 0.5 or 1 L volume) which is supposed to be representative for a commercial packaging provided that the special scale-up criteria is fulfilled.

The detailed analysis of these tests and scale-up procedures in use can be found in [5]. Specifically it was shown that the scale-up method proposed by the TDG for the H.4 test has been designed for liquids and only with certain modifications (e.g., proposed by Grewer [6] and Bowes [7]) can be applied for determining the SADT for packages with solid products of up to approximately 30 L.

The general way of resolving numerous problems dealing with determination of SADT for solids, particularly in the case of complex reaction kinetics, complex geometries, prediction of SADT for big packages or tanks, is the kinetics-based simulation, which can be very beneficial addition to the TDG tests.

Abbreviations: TDG, UN recommendations on the transport of dangerous goods, manual of tests and criteria; GHS, globally harmonized system of classification and labeling of chemicals; ADR, European agreement concerning the international carriage of dangerous goods by road; REACH, European Union regulation concerning the registration, evaluation, authorization and restriction of chemicals; SADT, the self accelerating decomposition temperature; DSC, differential scanning calorimeter.

* Corresponding author. Fax: +7 812 647 92 52.
E-mail addresses: kossoy@cisp.spb.ru (A.A. Kossoy), belohvostov@cisp.spb.ru (V.M. Belokhvostov), koludarova@cisp.spb.ru (E.Y. Koludarova).

http://dx.doi.org/10.1016/j.tca.2015.06.008
0040-6031/

Nomenclature

c_p	Specific heat capacity at constant pressure, kJ/kg/K
E_z	Effective activation energy, J/mol; describes temperature dependency of z
E	Activation energy, J/mol
k	Rate constant of a stage
k_0	Pre-exponent, 1/s
M	Mass, kg
n	Reaction order dimensionless
t	Time, s
T	Temperature, K
Q	Specific heat generation, J/g
R	Universal gas constant, $R = 8.314$ J/mol/K
r	Rate of a stage, 1/s
S	Surface of heat exchange, m^2
U	Heat transfer coefficient, $W/m^2/K$
U_s	Specific heat loss, mW/kg/K; $U_s = US/M$
W	Specific heat release rate; W/g
z	Autocatalytic parameter, dimensionless
z_0	Pre-exponent of the expression that describes temperature dependency of z
α,β,γ	Conversions; dimensionless
λ	Thermal conductivity coefficient, W/m/K
ρ	Density, kg/ m^3

Indices
s Surface
e Environment
o Value at $t = 0$

This approach comprises three main steps: implementing necessary series of lab-scale calorimetric experiments; creating the mathematical model of a reaction based on experimental data; incorporating the kinetic model into the model of an object (packaging, tank, etc.) and predicting its behavior by mathematical simulation. Application of this approach for more general task of evaluating thermal explosion hazard has been discussed, e.g., in [8,9]. Now its merits being applied to the SADT determination find wider recognition, which is illustrated by increasing number of publications (e.g., [5,10–12] to cite a few).

The main problem that impedes wider introduction of simulation methods into the research practice is that their experimental verification is absolutely necessary to prove the correctness of the approach. Fulfillment of this important step is hampered by the lack of thorough experimental data. Indeed the typical situation is that either data of lab-scale experiments for certain substance and a kinetic model are available without the results of the TDG tests or the results of the SADT determination by the TDG tests are reported without any information about reaction kinetics. From this viewpoint the project proposed by the Federal Institute for Materials Research and Testing, BAM, with this very purpose of verifying the simulation methods of the SADT determination based on thermal decomposition of 2,2′-azobis (isobutyronitrile), AIBN, as the benchmark was of significant importance. BAM has performed calorimetric study of AIBN decomposition and implemented series of large-scale H.1 and H.4 tests (M. Malow, K-D. Wehrstedt, M. Manolov, Thermal decomposition of AIBN: Part A: Decomposition in real scale packages and SADT determination, to be published). Then all these data have been distributed among the 3 participants of the project: ChemInform St. Petersdug Ltd., CISP, (Russia), Advanced Kinetics and Technology Solutions, AKTS, (Switzerland), and NETZSCH (Germany) for kinetics evaluation, simulation under condition of the H.1 and H.4 tests and prediction of the SADT. This article presents the results achieved by CISP.

2. Kinetics evaluation

2.1. Analysis of calorimetric data

The characterization of the AIBN samples studied and the details of calorimetric experiments implemented by BAM can be found in (M. Malow, K-D. Wehrstedt, M. Manolov, Thermal decomposition of AIBN: Part A: Decomposition in real scale packages and SADT determination, to be published). Here we present only necessary information relevant to further discussion.

AIBN is the solid crystal organic substance with melts at 103 °C. It decomposes exothermically in the solid state below melting point; after melting reaction accelerates significantly. This imposes restrictions on the experiment conditions. It is known that the SADT for 50 kg package with AIBN is about 50 °C therefore the solid-state decomposition is responsible for thermal explosion so that calorimetric study must be carried out below melting temperature, which excluded time-saving scanning experiments. Calorimetric data were collected in the course of several isothermal experiments. Due to limited sensitivity of the instrument used for experimental study the temperature interval

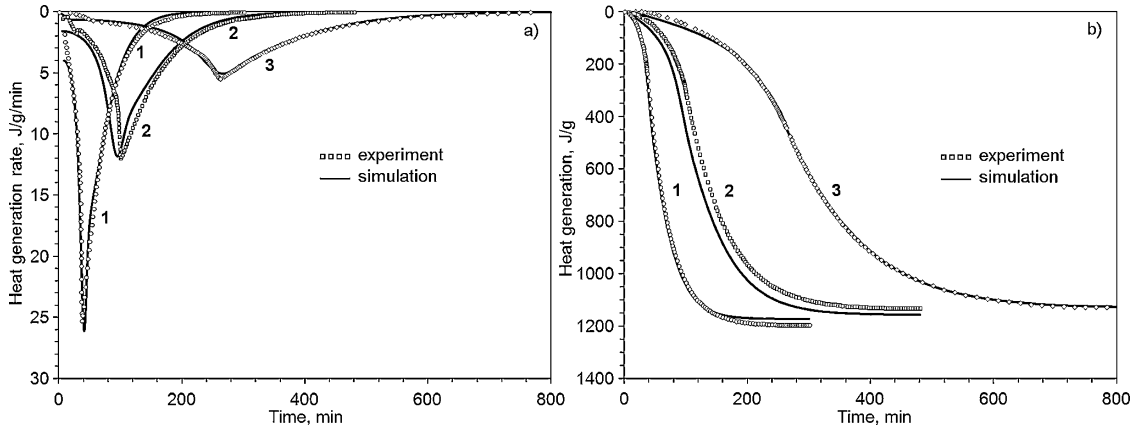

Fig. 1. Calorimetric data on solid-state decomposition of AIBN.
(a) heat production rate; (b) heat generation.
1: 90 °C; 2: 85 °C; 3: 80 °C.

Please cite this article in press as: A.A. Kossoy, et al., Thermal decomposition of AIBN: Part D: Verification of simulation method for SADT determination based on AIBN benchmark, Thermochim. Acta (2015), http://dx.doi.org/10.1016/j.tca.2015.06.008