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LETTER TO THE EDITOR

Further explanations of lauroyl peroxide runaway reaction by DSC tests and simulations

Answer to the critics of Prof. K.-D. Wehrstedt and Prof. M. Malow

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It is our honor and pleasure to discuss some phenomena of specific organic peroxide with Prof. M. Malow and Prof. K. D. Wehrstedt.

The kinetic parameters of the thermal behavior of lauroyl peroxide (LPO) were detected by DSC under non-isothermal conditions. Kinetic models and algorithms for thermal analysis were invented by Kossoy, Akhmetshin, and their associates (2007) of the Thermal Safety Software (TSS) [1–6]. Inputting experimentally derived data of interest into TSS is a simple analytical process that can be used to estimate or predict the thermal hazard of organic peroxides and other energetically sensitive materials to achieve optimization in the safety approaches of chemical plants. In our laboratory, many applied cases [7–10] in the use of organic peroxides and energetic materials have already been studied using this method. For instance, from Tables 1 and 2, the kinetic parameters of the thermal behavior of LPO were tested by DSC in non-isothermal conditions (with heating rates of 1, 2, 4, and 10 °C min^{-1}) first. Then they were further simulated using TSS by *n*th order and autocatalytic reaction processes, respectively.

In addition, the thermal hazard parameters of LPO, time to maximum rate (TMR), and a certain time to conversion limit (TCL) at heating rates of 1, 2, 4, and 10 °C min^{-1} by *n*th order and autocatalytic simulation were shown in Figs. 1 (for TMR) and 2 (for TCL). Under adiabatic condition, TMR is normally employed as a critical index of a temperature with an explosive accident potential once over by the surrounding temperature. According to Fig. 1, through simulation of a temperature of 70 °C, the TMR value was about 3–5 min. Utilization of this data could enable an operator to know how much time would be available for emergency response in the event of a runaway reaction. LPO is solid organic peroxide, belonging to the group of quasi-autocatalytic reactions of thermal decomposition [11]. When LPO was stored under isothermal conditions, over a long time, an abrupt self-heating of the resultant liquid started. In essence, exothermic decomposition reactions can begin when the solid and liquid phases coexist on one container [12].

Another parameter for determining thermal stability, which is characterized by the time necessary to reach TCL, was necessary to determine the stability of materials under storage or transportation conditions.

In our previous studies associated with the aforementioned kinetic-based simulation approach, three main steps were conducted: executing a necessary series of calorimetric experiments; building up the mathematical model of a reaction based on experimental data of DSC, incorporating the kinetic model into the model of processing; and achieving the practical target by applying mathematical simulations. In case of a package containing a solid with both internal heat losses from the surface are important [6].

Various vessel types with different material densities were chosen for simulation, like LPO in box is simulated by solid thermal explosion specifying boundary conditions of the first, second, and third type. Transport package sizes and boundary conditions, shown in Tables 3 and 4, were assumed to be uniform over each package's surface.

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Compared to small-scale tests of US self-accelerating decomposition temperature (SADT), our results were similar or the same. The SADT is an important measurement that characterizes thermal safety for transport of self-reactive substances. From the simulations [1–6], the different package sizes of box 1 and box 2 were displayed in Tables 5 and 6. We found that the simulation results varied from the experimental results. In contrast, the simulation was able to predict how variation of geometry, physical properties, and features of a reaction can affect reliability of the results. In addition, in our simulations by TSS, any variation of heat was assumed to be observed at the central point inside the box. Any non-uniformity of a system resulted in significant differences in the SADT, but specifically, non-uniformity packages will make the diminution of thermal conductivity results in lowering of the SADT [6].

To find thorough solutions to the problems indicated by Profs. Malow and Wehrstedt, we have been consulting with Dr. Kossoy, who is in charge of the TSS tool development, for his valuable technical supports regarding their criticisms. The following statements are personal communications from Dr. Kossoy:

> "In fact Dr. Malow and Dr. Wehrshtedt cite the results and experience that refer to the solid LPO whereas the estimates given in the paper are attributed to liquid. Apparently LPO in solid phase is much more stable than in liquid phase therefore the results form the paper (TMR and SADT) are just incomparable with that mentioned in the letter even provided that decomposition kinetics (for liquid) evaluated from DSC experiments is adequate and all the simulations have been performed correctly.
> Additional remark is that DSC is not appropriate for investigation of the "solid scenario" which is of significant practical interest as LPO is stored and transported in solid phase. For this purpose, solid decomposition had to be studied using TAM at low temperatures in isothermal mode—at least initial stage of decomposition. In this case DSC can give reasonable estimate of total heat of reaction."

We are deeply thankful for the valuable comments and questions from Profs. Malow and Wehrstedt. The journal article they criticize originally dealt with the crucial thermokinetic parameters of LPO found experimentally via use of DSC, emphasizing the newly discovery of SADT and TMR. With respect to the simulation evaluation of LPO, although we have been applied great effort to pursuit of the minimum variation between the results of simulation and experimental approaches, due to our unfamiliarity with the TSS simulations at that time, it is possible that some parameter settings may not have been adequate, in effect causing the differences in simulated results from those of Profs. Malow and Wehrstedt. We would like to offer our apology to Prof. Malow, Prof. K. D. Wehrstedt, and Prof. J. Simon (the Editor-in-Chief of JTAC) for any unwitting mistakes in our simulations. In future, we will do our best possible to look strictly over our studies applying these simulations in the interests of correct methods for safety approaches and protocols of chemical plants.

References

1. Kossoy AA, Hofelich T. Methodology and software for reactivity rating. Process Saf Prog. 2003;22(4):235–40.
2. Kossoy AA, Benin AI, Akhmetshin YG. An advanced approach to reactivity rating. J Hazard Mater. 2005;118(1–3):9–17.
3. Kossoy AA, Akhmetshin YG. Identification of kinetic models for the assessment of reaction hazards. Process Saf Prog. 2007;26(3):209–20.
4. Thermal Safety Software (TSS), ChemInform Saint-Petersburg (CISP) Ltd., St. Petersburg, Russia. http://www.cisp.spb.ru.
5. Kossoy AA, Sheinman YI. Evaluating thermal explosion hazard by using kinetics-based simulation approach. Process Saf Environ Protect. 2004;82(B6):421–30.
6. Kossoy AA, Sheinman YI. Comparative analysis of the methods for SADT determination. J Hazard Mater. 2007;142:626–38.
7. Lin CP, Chang CP, Chou YC, Chua YC, Shu CM. Modeling solid thermal explosion containment on reactor HNIW and HMX. J Hazard Mater. 2010;176:549–58.
8. Lin CP, Chang YM, Tseng JM, Shu CM. Comparisons of *n*th-order kinetic algorithms and kinetic model simulation on HMX by DSC tests. J Therm Anal Calorim. 2010;100(2):607–14.
9. Wu SH, Shyu ML, YP I, Chi JH, Shu CM. Evaluation of runaway reaction for dicumyl peroxide in a batch reactor by DSC and VSP2. J Loss Prev Process Ind. 2009;22(6):721–7.
10. Chen KY, Wu SH, Wang YW, Shu CM. Runaway reaction and thermal hazards simulation of cumene hydroperoxide by DSC. J Loss Prev Process Ind. 2008;21:101–9.
11. Kotoyori T. The self-accelerating decomposition temperature (SADT) of solids of the quasi-autocatalytic decomposition type. J Hazard Mater. 1999;64:1–19.
12. Li XR, Koseki H. Thermal decomposition kinetic of reactive solid based on isothermal calorimetry measurements. J Therm Anal Calorim. 2006;85(3):637–42.