



## Publications of the TSS software users

1. **H. Johnstone, Evaluation of reaction hazards for a wiped-film evaporator, Process Safety Progress, 2002, V 21 Issue 4, 313 – 321**

### Abstract

To increase its capacity, a production plant investigated raising the operating temperature of a wiped-film evaporator (WFE) unit. The WFE separates a high-boiling product (taken overhead) from a heavy tar stream (taken out the bottom). Both product and tars begin to decompose at temperatures near the operating temperature of the WFE. The plant's Management of Change procedure required that all potential reactivity hazards be considered before making the proposed change. This paper describes the experimental work done on plant samples with ARC and Setaram C-80 instruments, and how decomposition kinetic parameters were estimated using thermal safety software from Cheminform St. Petersburg, Ltd. The results of this hazard evaluation allowed the plant personnel to make an informed decision about the proposed operating change

2. **A.A. Aldeeb, Systematic approach for chemical reactivity evaluation, PhD dissertation, Texas A&M University, US, 2003**

### Abstract.

Under certain conditions, reactive chemicals may proceed into uncontrolled chemical reaction pathways with rapid and significant increases in temperature, pressure, and/or gas evolution. Reactive chemicals have been involved in many industrial incidents, and have harmed people, property, and the environment.

Evaluation of reactive chemical hazards is critical to design and operate safer chemical plant processes. Much effort is needed for experimental techniques, mainly calorimetric analysis, to measure thermal reactivity of chemical systems. Studying all the various reaction pathways experimentally however is very expensive and time consuming. Therefore, it is essential to employ simplified screening tools and other methods to reduce the number of experiments and to identify the most energetic pathways.

A systematic approach is presented for the evaluation of reactive chemical hazards. This approach is based on a combination of computational methods, correlations, and experimental thermal analysis techniques. The presented approach will help to focus in the experimental work to the most hazardous reaction scenarios with a better understanding of the reactive system chemistry.

Computational methods are used to predict reaction stoichiometries, thermodynamics, and kinetics, which then are used to exclude thermodynamically infeasible and non-hazardous reaction pathways. Computational methods included: (1) molecular group contribution methods, (2) computational quantum chemistry methods, and (3) correlations based on thermodynamic-energy relationships. The experimental techniques are used to evaluate the most energetic systems for more accurate thermodynamic and kinetics parameters, or to replace inadequate numerical methods.

The Reactive System Screening Tool (RSST) and the Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) were employed to evaluate the reactive systems experimentally. The RSST detected exothermic behavior and measured the overall liberated energy. The APTAC simulated near-adiabatic runaway scenarios for more accurate thermodynamic and kinetic parameters.

The validity of this approach was investigated through the evaluation of potentially hazardous reactive systems, including decomposition of di-tert-butyl peroxide, copolymerization of styrene-acrylonitrile, and polymerization of 1,3-butadiene.

3. **D. Cancellieri, E. Leoni, J.L. Rossi, Kinetics of the thermal degradation of Erica arborea by DSC: Hybrid kinetic method, Thermochimica Acta 438 (2005) 41–50**

### Abstract

The scope of this work was the determination of kinetic parameters of the thermal oxidative degradation of a Mediterranean scrub using a hybrid method developed at the laboratory. DSC and TGA were used in this study under air sweeping to record oxidative reactions. Two dominating and overlapped exothermic peaks were recorded in DSC and individualized using an experimental and numerical separation. This first stage allowed obtaining the enthalpy variation of each exothermic phenomenon. In a second time, a model free method was applied on each isolated curve to determine the apparent activation energies. A reactional kinetic scheme was proposed for the global exotherm composed of two independent and consecutive reactions. In fine mean values of enthalpy variation and apparent activation energy previously determined were injected in a model fitting method to obtain the reaction order and the preexponential factor of each oxidative reaction. We plan to use these data in a sub-model to be integrated in a wildl and fire spread model.

4. **R. H. Chang, J. M. Tseng, J. M. Jehng, C. M. Shu, H. Y. Hou, Thermokinetic model simulations for methyl ethyl ketone peroxide contaminated with H<sub>2</sub>SO<sub>4</sub> or NaOH by DSC and VSP 2, , Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 1, 57–62**

#### **Abstract**

In this study, a mixture of methyl ethyl ketone peroxide (MEKPO) with various contaminants, such as H<sub>2</sub>SO<sub>4</sub> and NaOH, was prepared in order to elucidate the cause of these accidents and the results of upset conditions. Thermokinetic parameters were acquired by both differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). In addition, we simulated the thermokinetic parameters and created kinetic models for the specific contaminants. The results indicate that the thermal hazard of MEKPO is less than that of the mixed MEKPO with the above-mentioned contaminants. Consequently, the evaluated parameters could be used to prevent any unexpected exothermic runaway reaction or to alleviate hazards to an acceptable extent, if such a reaction occurs.

5. **S. Fischer, G. Krahn, B. Reimer, Evaluation of microcalorimetric measurements in terms of information content for decomposition reactions, Thermochimica Acta, Volume 445, Issue 2, 15 June 2006, Pages 160-167**

#### **Abstract**

Decomposition reactions of liquids and solids can be observed by the heat development using microcalorimetric methods. By determination of the released heat flow for heating up a sample, it is possible to get details to answer safety relevant questions.

For reactions nth order the overall activation energy and the accompanying frequency factor can be determined, provided that the heat release is determined by the rate of a single reaction step. Researches have been carried out whether these parameters are useable for safety technical specifications.

Autocatalytic affected decomposition reactions are connected with special problems. This affects the experimental examination or interpretation of results, and also the precise identification of beginning decomposition reactions in technical reactors. The application of microcalorimetric measurements on decomposition reactions is described and associated problems are pointed out.

The conclusions from thermoanalysis data alone are not sufficient in the final consequence for safety technical assessments.

6. **K. W. Wu, H. Y. Hou, C. M. Shu, Thermal phenomena studies for dicumyl peroxide at various concentrations by DSC, Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 1, 41–44**

#### **Abstract**

Information about the kinetics and thermal decomposition of dicumyl peroxide (DCPO) is required for safety concerns, due to its wide applications and accident cases. To understand the inherent hazards during DCPO manufacturing, we selected various concentrations in different stages and analyzed them by differential scanning calorimetry (DSC). We evaluated thermokinetic parameters to set up a simple, but comprehensive kinetic model, with various tests conducted at heating rates of 2, 4, 6 and 10°C/min. Subsequently, we established a more efficient, resource-effective, and cost-effective model of safety evaluation for DCPO with different concentrations, according to thermokinetic parameters, such as activation energy  $E_a$  is 125.35 kJ/mol, frequency factor  $k_0$  is  $3.124 \cdot 10^{12}$  1/s, reaction order  $n$  is 0.9 and heat of decomposition  $\Delta H$  is 750.52 J/g for DCPO 99 mass%.

7. **Ch. Zhang, Thermal decomposition study of hydroxylamine nitrate during storage and handling, master thesises, Texas A&M University, US, 2006**

#### **Abstract.**

Hydroxylamine nitrate (HAN), an important agent for the nuclear industry and the U.S. Army, has been involved in several costly incidents. To prevent similar incidents, the study of HAN safe storage and handling boundary has become extremely important for industries. However, HAN decomposition involves complicated reaction pathways due to its autocatalytic behavior and therefore presents a challenge for definition of safe boundaries of HAN storage and handling.

This research focused on HAN decomposition behavior under various conditions and proposed isothermal aging testing and kinetic-based simulation to determine safety boundaries for HAN storage and handling. Specifically, HAN decomposition in the presence of glass, titanium, stainless steel with titanium, or stainless steel was examined in an Automatic Pressure Tracking Adiabatic Calorimeter (APTAC).  $n$ -th order kinetics was used for initial reaction rate estimation. Because stainless steel is a commonly used material for HAN containers, isothermal aging tests were conducted in a stainless steel cell to determine the maximum safe storage time of HAN. Moreover, by changing thermal inertia, data for HAN decomposition in the stainless steel cell were examined and the experimental results were simulated by the Thermal Safety Software package.

This work offers useful guidance for industries that manufacture, handle, and store HAN. The experimental data acquired not only can help with aspects of process safety design, including emergency relief systems, process control, and process equipment selection, but also is a useful reference for the associated theoretical study of autocatalytic decomposition behavior.

8. **S. Fisher, Characterization of exothermal decomposition with thermoanalytical and numerical reactions methods, BASF, internal report. 2008**

#### **Abstract**

The aim of the chemical industry is to minimise the risk during handling, storage and transportation of materials. Usually the chemical synthesis reactions of the desired product are well-known and exothermic processes can be controlled. It has to be checked if in case of process deviations during production of the material an unwanted decomposition reaction with strong heat of reaction and high pressure and temperature rise can occur. Certain specific hazards result from decomposition reactions, which proceed according to an autocatalytic type of reaction. Accordingly, it is important to distinguish between autocatalytic reaction and reaction nth – order. The differential scanning calorimetry (DSC) has been used as a screening method. The aim is to point out differences between the autocatalytic decomposition mechanism and the nth – order on the basis of DSC measurements. A procedure is introduced to determine the reaction type of decomposition. Numerical methods are applied for kinetic analysis of dynamic and isoperibolic tests and the simulation results of the ADT24. The results are tabled hereunder.

9. **M. Bernhart, O. Fasina, Properties of Fractionated Poultry Litter, Auburn University, Auburn, AL, Presentation at the 2008 ASABE Annual Int. Meeting, Providence, Rhode Island, 2008**

#### **Abstract.**

Due to environmental issues with the use of poultry litter for land application, alternative means for its value added utilization need to be identified. One possible solution is the fractionating of poultry litter into a nutrient rich fine fraction that can be used as fertilizer and a coarser fraction that has the potential of being used as bioenergy feedstock. In this study, physical properties relevant to storage, handling and processing of poultry litter that were separated into three fractions (with average diameters of 0.396, 0.708 and 1.181 mm) were determined. The densities (bulk, particle and tap) of the fractions increased with fraction size. The fine fraction was the most compressible and was the dominant contributor to the compressibility of unfractionated poultry litter. Coarse fraction was the least compressible. The flow index values of the coarse, middle and fine fractions were 16.1, 13.2 and 11.5 respectively and were significantly higher than the flow index of unfractionated poultry litter (3.6). The heating value, the carbon content and the rate of thermal decomposition of the fractions increased with increase in particle size of the fractions. Maximum thermal decomposition rates of 0.107 1/min, 0.126 1/min, 0.154 1/min were obtained for the fines, middle and coarse fractions respectively.

10. **S-B. Lee, O. Fasina, TG-FTIR Analysis of Switchgrass Pyrolysis, Auburn University, Auburn, AL, Presentation at the 2008 ASABE Annual Int. Meeting, Providence, Rhode Island, 2008**

#### **Abstract.**

Switchgrass is a high yielding perennial grass that has been designated as a potential energy crop. One method of converting switchgrass to energy is by thermochemical conversion to syngas. This requires that the rate of thermal decomposition of switchgrass and the rate of production of components of the syngas be quantified. Ground switchgrass were pyrolysed at heating rates of 10C/min to 40C/min in a thermogravimetric analyzer coupled to a Fourier transform infrared spectrometer. The amount of gases (ppm) that were volatilized during the duration of experiment were quantified. The pyrolysis process was found to compose of four stages: moisture evaporation, hemicellulose decomposition, cellulose decomposition and lignin degradation. The peak temperature for hemicellulose (288C to 315C) and cellulose degradation (340C to 369C) increased with heating rate. FTIR analysis showed that the following gases were given off during the pyrolysis of switchgrass: carbon dioxide, carbon monoxide, acetic acid, ethanol, and methane.

11. **Kun-Yue Chen, Sheng-Hung Wu, Yih-Wen Wang, and Chi-Min Shu, Runaway reaction and thermal hazards simulation of cumene hydroperoxide by DSC, Journal of Loss Prevention in the Process Industries, V 21, Issue 1, 2008, 101-109**

#### **Abstract**

A simplified self-heating rate equation was developed to simulate the adiabatic thermal hazards of 88 mass% cumene hydroperoxide (CHP) in cumene. CHP has been predominantly used

in producing phenol and acetone by catalytic cleavage and as initiator in the acrylonitrile–butadiene–styrene (ABS) copolymer polymerization process. In this study, we acquired experimental data, such as the heat of decomposition ( $\Delta H_d$ ) and exothermic onset temperature (TO) by differential scanning calorimetry (DSC). The data were, in turn, used

to simulate a runaway reaction and thermal analysis on 88 mass% CHP under various scenarios. The thermal safety software (TSS) series was employed to evaluate reaction kinetics, to simulate the runaway excursion of interest and to allow determination of critical conditions

or thermal explosion of the tank. The liquid thermal explosion (LTE) model to simulate thermal explosion of CHP is aimed at ensuring safe storage or transportation. The reliability of both model simulations was assessed by experimentally comparing the thermal hazards with DSC. This simplified methodology is a sound, efficient tool for thermal hazards assessment of energetic chemicals.

12. **Y. -P. Chou, J. -Y. Huang, J. -M. Tseng, S. -Y. Cheng and C. -M. Shu, Reaction hazard analysis for the thermal decomposition of cumene hydroperoxide in the presence of sodium hydroxide Journal of Thermal Analysis and Calorimetry, V 93, N 1, 2008, 275-280**

#### **Abstract**

Organic peroxides have caused many serious explosions and fires that were promoted by thermal instability, chemical pollutants, and even mechanical shock. Cumene hydroperoxide (CHP) has been employed in polymerization and for producing phenol and dicumyl peroxide (DCPO). Differential scanning calorimetry (DSC) has been used to assess the thermal hazards associated with CHP contacting sodium hydroxide (NaOH). Thermokinetic parameters, such as exothermic onset temperature ( $T_0$ ), peak temperature ( $T_{max}$ ), and enthalpy ( $\Delta H$ ) were obtained. Experimental data were obtained using DSC and curve fitting using thermal safety software (TSS) was employed to obtain the kinetic parameters. Isothermal microcalorimetry (thermal activity monitor, TAM) was used to investigate the thermal hazards associated with storing of CHP and CHP mixed with NaOH under isothermal conditions.

TAM showed that in the temperature range from 70 to 90°C an autocatalytic reaction occurs. This was apparent in the thermal curves. Depending on the operating conditions, NaOH may be one of the chemicals or catalysts incompatible with CHP. When CHP was mixed with NaOH, the  $T_0$  is lower and reactions become more complex than those associated with assessment of the decomposition of the pure peroxide. The data by curve fitting indicated that the activation energy ( $E$ ) for the induced decomposition is smaller than that for decomposition of CHP in the absence of hydroxide.

13. **A.Yu. Snegirev, V.A. Talalov, V.V., Stepanov, J.N. Harris, Formal kinetics of polystyrene pyrolysis in non-oxidizing atmosphere, Thermochemica Acta 548 (2012) 17–26**

#### **Abstract.**

Previously reported kinetic data on polystyrene thermal degradation are inconsistent, and this may be a potential source of error in modeling the ignition and burning of the polymer composite materials containing polystyrene. To derive formal kinetic model of polystyrene thermal degradation, pyrolysis combustion flow calorimetry (PCFC) has been applied in this work.

The heat release rate-temperature dependencies were measured at four heating rates of 0.25, 0.5, 1.0 and 2.0 C/s under nitrogen flow, and the kinetic parameters were derived by means of the model-free isoconversional method, the peak value method, the method of Kissinger and the model fitting non-linear optimization method.

The single-step global reaction model has been demonstrated to have a constant activation energy of 168 kJ/mol in a wide range of conversions. The autocatalytic reaction type has been established by evaluating the dependence of the kinetic function on the conversion derived from the measurement data. Then developed kinetic model has been validated against a variety of data sets including PCFC measurements made in this work, published TGA measurements, and isothermal experimental data.

The model reproduced the experimental data to a reasonable accuracy for different temperature programs. The  $n$ th order reaction model was demonstrated to be unable to predict reaction rates for a range of different heating rates although it could be optimized for a single temperature program. Use of the  $n$ th order reaction has been shown to be reason of obtaining unrealistically high apparent activation energies, reported for polystyrene degradation in the literature. The importance of processing multiple heating rate data to avoid misleading results is highlighted.

14. **Kuang-Hua Hsueh, Wei-Chun Chen, Wei-Ting Chen, Chi-Min Shu, Thermal decomposition analysis of 1,1-bis(tert-butylperoxy)cyclohexane with sulfuric acid contaminants. Journal of Loss Prevention in the Process Industries, 40 (2016) 357e364.**

#### **Abstract.**

Owing to the thermally unstable 1,1-bis(tert-butylperoxy)cyclohexane (BTBPC) having two active O-O peroxide group, it is a thermal instability material. It is usually used as an initiator in radical polymerization. This study focused on the runaway reactions of BTBPC alone and mixed with various concentrations of sulfuric acid ( $H_2SO_4$ ) (1.0, 2.0, 4.0, and 8.0 N). The essential thermal stability kinetic parameters, such as exothermic onset temperature ( $T_0$ ), peak temperature ( $T_p$ ), apparent activation energy ( $E_a$ ), heat of decomposition ( $\Delta H_d$ ), and rate constant ( $k$ ), were evaluated by differential scanning calorimetry (DSC) at the heating rate of 4.0 C/min between 30.0 and 300.0 C. A kinetics-based curve fitting method was employed to assess the thermal stability kinetic parameters and possible reaction scheme.  $H_2SO_4$  appears to inhibit the decomposition reaction of BTBPC, especially when BTBPC is mixed with 8.0 N  $H_2SO_4$ .

15. **Steffen H. Duerrstein, Claudia Kappler, Isabel Neuhaus, Marcus Malow, Michael-Schulz, Markus Gödde, Model-Based Prediction of the Adiabatic Induction Period and SADT of Dicumyl Peroxide Solution and Comparison to Large-Scale Experiments Performed Using 216.5-Liter Steel Drums in the UN-Test H.1, Chemical Engineering Transactions, Vol. 48, 2016, 475-480**

#### **Abstract.**

The thermal decomposition of dicumyl peroxide dissolved in ethylbenzene has been studied in our laboratories using differential scanning calorimetry (DSC), Calvet calorimetry (C80), adiabatic calorimet-

ry, reaction calorimetry and micro calorimetry. Based on the DSC and C80 experiments a formal kinetics model has been derived, which was compared to the other applied techniques. Finally we used our model to predict the thermal response of 216.5 L steel drums to exposure to constant elevated temperatures, both using the stationary Semenov approach as well as time-resolved CFD simulations. The prediction was compared to one-to-one testing using the UN-Test H.1. The observed level of consistency between model and experiments is remarkably good. The comparison with the 216.5 L testing clearly demonstrates that reliable and conservative predictions for technically relevant scales are possible as long as a validated model is used.

16. **Shun-Yao Wang, Arcady A. Kossoy, Ya-Dong Yao, Li-Ping Chen, Wang-Hua Chen, Kinetics-based simulation approach to evaluate thermal hazards of benzaldehyde oxime by DSC tests, *Thermochimica Acta* 655 (2017) 319–325**

**Abstract.**

To evaluate thermal hazards of benzaldehyde oxime (BO), dynamic experiments were carried out by differential scanning calorimeter (DSC) to obtain thermodynamic parameters. A kinetic model was evaluated by fitting experimental curves. Finally, thermal behaviors under isothermal, adiabatic and conditions of limited intensity of heat exchange were simulated. The results indicate that BO decomposes rapidly in liquid phase, and releases a large amount of thermal energy. The reaction model of full autocatalysis has been created comprising two parallel stages: initiation stage of the n-order type, and the autocatalytic stage. Contribution of the two stages are also presented. Simulation results demonstrate low stability of BO in liquid phase, it decomposes at low temperature right above melting and results in thermal explosion even for a small container. Estimation of time to maximum rate (TMR ad ) demonstrates the operational temperature should not be higher than 42 °C during production and usage.

17. **Ze Dong, Li-ping Chen, Ying-ying Ma, Hao-liang Peng, Wang-hua Chen, Adiabatic Correction for the Esterification of Acetic Anhydride by Methanol via Accurate Kinetics, *Chinese Journal of Chemical Engineering*, 2017, DOI: 10.1016/j.cjche.2017.10.005**

**Abstract.**

In the field of adiabatic correction for complex reactions, a simple one-stage kinetic model was used to estimate the real reaction kinetics. However, this assumption simplified the real process, inevitably generated inaccurate or even unsafe results. Therefore, it was necessary to find a new correction method for complex reactions. In this work, esterification of acetic anhydride by methanol was chosen as an object reaction of study. The reaction was studied under different conditions by Reaction Calorimeter (RC1). Then, Thermal Safety Software (TSS) was used to establish the kinetic model and estimate the parameters, where, activation energies for three stages were 67.09, 81.02, 73.77 kJ/mol respectively, and corresponding frequency factors in logarithmic form were 16.05, 19.59, 15.72 1/s. In addition, two adiabatic tests were performed by Vent Sizing Package2 (VSP2). For accurate correction of VSP2 tests, a new correction method based on Enhanced Fisher method was proposed. Combined with kinetics, adiabatic correction of esterification reaction was achieved. Through this research, accurate kinetic parameters for a three-step kinetic model of the esterification reaction were acquired. Furthermore, the correlation coefficients between simulated curves and corrected curves were 0.976 and 0.968, which proved the accuracy of proposed new adiabatic correction method. Based on this new method, conservative corrected results were able to be acquired and be applied in safety assessment.

18. **Yang-Fan Cheng, Shang-Hao Liu, Chi-Min Shu, Bin Zhang, Yun-Fei Li, Energy estimation and modeling solid thermal explosion containment on reactor for three organic peroxides by calorimetric technique, *J Therm Anal Calorim* (2017) 130:1201–1211**

**Abstract.**

In this paper, we describe thermokinetic properties and decomposition characteristics of benzoyl peroxide, dicumyl peroxide, and lauroyl peroxide, which are widely used in the polymerization process as energy boosters. In the past, many accidents occurred that involved overpressure and runaway excursion of the process and thermal explosion. One reason for accidents is because of the peroxy group (–O–O–) of organic peroxides (OPs) due to its thermal instability and high sensitivity when exposing to heat. Apparent activation energy and preexponential factor were obtained during decomposition via non-isothermal well-recognized kinetic equation, fitting curve tests, and approximate solution to design safer reaction conditions when OPs are used as fuel. Moreover, the storage conditions were investigated for the simulation of thermal explosion in a 24-kg cubic box package and a 400-kg barrel reactor for commercial application.

19. **Ruichao Wei, Shenshi Huang, Zhi Wang, Richard Yuen, Jian Wang, Evaluation of the critical safety temperature of nitrocellulose in different forms, *Journal of Loss Prevention in the Process Industries* 56 (2018) 289–299**

**Abstract.**

Evaluating the critical safety temperature of nitrocellulose is necessary to reduce the possibility of nitrocellulose accidents (thermal explosion and fire) and to implement effective loss prevention. In the present study, isothermal and non-isothermal experiments were performed on different forms of

nitrocellulose using a differential scanning calorimeter. A scanning electron microscope was utilized to detect the aging process of nitrocellulose under different constant temperatures. Thermodynamic parameters were simulated by thermal safety software, and the results indicated that autocatalytic simulation rather than nth order simulation was applicable to assess the apparent activation energy of nitrocellulose samples. Moreover, iso-conversional methods, including Kissinger–Akahira–Sunose, Ozawa–Flynn–Wall, Friedman, Tang et al. and distributed activation energy model methods, were employed to validate the simulated activation energy.

The average activation energy calculated by the five iso-conversional methods was lower than that simulated by autocatalytic simulation. Moreover, critical storage temperatures, including the time to maximum rate and the time to conversion limit, were evaluated. It was found that the critical storage temperatures of nitrocellulose in white chip form were lower than that of nitrocellulose in white silky fibre form. Finally, the critical thermal explosion temperatures of two samples were calculated, and it was concluded the temperature of nitrocellulose in white silky fibre form was about 5.0 °C higher than that of nitrocellulose in white chip form.

20. **Rui Chao Wei, Shen Shi Huang, Zhi Wang, Yu He, Richard Yuen, Jian Wang, Estimation on the Safe Storage Temperature of Nitrocellulose with Different Humectants, Propellants, Explos. Pyrotech. 43, (2018), 1–8. <https://doi.org/10.1002/prep.201800149>**

#### **Abstract.**

In order to estimate the safe storage temperatures of nitrocellulose (NC) with different humectants (water, ethanol, and isopropanol), non- isothermal experiments were performed by a differential scanning calorimeter (DSC). Thermodynamic parameters were simulated by thermal safety software (TSS). Comparison of autocatalytic simulation and nth order simulation was conducted. Also, Kissinger- Akahira- Sunose (KAS) and Ozawa- Flynn- Wall (OFW) methods were employed to validate the simulated activation energy E, whose results indicated that the average E calculated by KAS and OFW methods is lower than that simulated by autocatalytic simulation. Finally, the critical temperatures of time to maximum rate (TMR) and time to conversion limit (TCL) were estimated. The results show that the critical temperature of pure NC is higher than that of NC with humectants, which indicates that NC with humectants possess a higher thermal instability at an identical temperature. In addition, to ensure the effectiveness of NC products, storage temperatures of pure NC and NC- humectants were also simulated.

21. **Lang Zhao, Ying Yin, Heliang Sui, Qian Yu, Shanhu Sun, Haobin Zhang, Shun Yao Wang, Liping Chen, Jie Sun, Kinetic model of thermal decomposition of CL-20/HMX co-crystal for thermal safety prediction, Thermochimica Acta 674 (2019) 44–51**

#### **Abstract.**

To promote the practical application of CL-20/HMX co-crystal, the understanding of its thermal decomposition kinetics and thermal hazard prediction are highly required. In this study, the kinetic model was evaluated based on the non-isothermal DSC data by using non-linear optimization method, which was identified as a complicated reaction comprising two parallel autocatalytic paths, and the contribution of the two reaction paths was revealed to vary depending on the heating rate. Based on the kinetic model, the thermal hazard simulation indicates that the temperature when the occurrence of thermal decomposition after 24 h ( $T_{d,24}$ ) of CL-20/HMX co-crystal is 151.64 °C, and the critical temperature of 1000th second explosion is determined as ~196 °C. Besides, simulation results of self-accelerating decomposition temperature demonstrate that the package mass of CL-20/HMX co-crystal, rather than the package material, has a remarkable effect on the thermal safety of CL-20/HMX co-crystal.

22. **Hua-Bo Li, Shun-Yao Wang, Xiao-Yu Gan, Wang-Hua Chen, Li-Ping Chen, Thermal risk analysis of benzoyl peroxide in the presence of phenol: Based on the experimental and simulation approach, Thermochimica Acta, V 681, 2019**

#### **Abstract.**

The thermal behaviors of benzoyl peroxide (BPO) under contamination have been a topic received extensive attention. This paper attempted to examine the effect of phenol on the decomposition reaction of BPO by applying dynamic, isothermal DSC experiments and slow cook-off test. A kinetic model was further established by the Thermal Safety Software through fitting DSC curves and verified by the slow cook-off test. Moreover, the runaway reactions under different storage conditions were predicted. The results indicate that the phenol significantly reduces the thermal stability of BPO and the Benito-Perez model is credible to evaluate the decomposition process. During simulating the reaction process, it is predicted that the explosion could take place even at the 40 °C for 50 kg packaging sample. For 10% limit value, the time to conversion limit of sample is 7.49 h at 40 °C, while it just only 2.37 h at 110 °C.

23. **Chen Li, Fengguo Ma, Jie Sun, Heliang Sui, Qian Yu, Lang Zhao, Ying Yin, Thermal hazard evaluation of N-guanylurea dinitramide (GUDN) by using kinetic-based simulation approach, Journal of Thermal Analysis and Calorimetry, 2019 (to be published)**

**Abstract.**

To promote the practical application of N-guanylurea dinitramide (GUDN), it is necessary to identify the thermal kinetics and evaluate the thermal safety of GUDN under various environmental conditions. In this study, we present that the thermal decomposition of GUDN is a typical autocatalytic reaction and the kinetic-based model was established by simultaneous fitting of a series of non-isothermal DSC data at different heating rates, which can be described as a generalized autocatalytic model, expressed as  $da/dt=2.29 \times 10^{23} \exp(-225.24/R/T)(1-a)^{1.76}(a^{1.47}+0.59 \exp(-18.3/R/T))$ . The reaction model exhibits a reasonable fitting to the experimental results with a high correlation coefficient  $R^2$  of 0.9994. Based on the established kinetic model, important thermal safety indicators, such as the time to conversion limit (TCL), adiabatic time to maximum rate (TMR ad), and self-accelerating decomposition temperature (SADT) were simulated, providing important basis concerning the thermal hazard of GUDN in practical applications.

24. **Fang Yang, Ya Chen, Chuande Zhao and Long Zhang, Studies on the thermal behavior and safety of a novel thermostable explosive BPTAP, RSC Advances (September 2019), DOI: 10.1039/c9ra03385h**

**Abstract.**

Thermal decomposition of a highly thermostable explosive dihydroxylammonium 2,4,8,10-tetraazobenzopyrido-1,3a,6,6a-tetraazapentalene (BPTAP) was studied using conventional thermal analysis techniques (Thermal Gravimetric Analysis and Differential Scanning Calorimetry). To obtain more comprehensive insight into the kinetics mechanism of BPTAP decomposition, thermoanalytical experiments were performed under non-hermetic and hermetic conditions. Several widely used thermoanalytical data processing techniques based on model-free kinetics (Flynn – Wall – Ozawa, Kissinger, Freidman, numerical optimization) were studied and compared. Furthermore, to fully understand the thermal safety property of BPTAP, the kinetic model and the kinetic parameters were evaluated based on the non-isothermal DSC data by using a non-linear optimization method. The kinetic models of thermal decomposition of BPTAP under non-hermetic and hermetic conditions were different, which were identified as the generalized autocatalysis reaction and two parallel generalized autocatalysis reactions, respectively. On the basis of the aforementioned study, two important safety parameters including the time to maximum rate under adiabatic conditions and self-accelerating decomposition temperature for BPTAP in DEWAR were calculated and discussed.

25. **Shang-Hao Liu, Chen-Rui Cao, Wei-Cheng Lin, Chi-Min Shu, Experimental and numerical simulation study of the thermal hazards of four azo compounds, Journal of Hazardous Materials 365 (2019) 164–177**

**Abstract.**

Azo compounds (azos) possess diverse exothermic properties that enable their application in numerous industrial processes, but these properties also engender a corresponding diversity of thermal hazard profiles. This study employed an innovative approach to determine the specific thermal reactions and decomposition hazard profiles of azos. Four typical azos (AIBN, AMBN, ABVN, and AIBME) were assessed using three thermal calorimetry techniques, and results were subsequently analyzed using a nonlinear optimization model. Thermal hazard analysis of small-scale experiments indicated that AIBN had a heat decomposition of 1247 J/g and a maximum pressure increase of 367 psig and thus exhibited more hazardous characteristics than did AMBN, ABVN, and AIBME.

This study also obtained the relevant process safety parameters, time to maximum rate, onset and peak temperature, adiabatic temperature rise, and rate of pressure increase to use for later scaled-up applications. The findings of this study can be used to develop a predictive model for the thermal behavior of azos and to provide the necessary basis for the design and selection of precise treatment and appropriate safety systems.

26. **Hong-Bo Wu, Shang-Hao Liu & Chen-Rui Cao, Influence and assessment of AIBN on thermal hazard under process situations, Journal of Thermal Analysis and Calorimetry (April 2020), DOI: 10.1007/s10973-020-09645-4**

**Abstract**

Free radical polymerization is an effective method for large-scale production of various olefin polymers, in which the initiator is one of the emphases in the study of different chain reaction mechanisms in chemical industry. The azo compounds are widely used in organic synthesis to initiate chain reactions. Azos are divided into different types according to the applicable temperature range. 2,2'-Azobis(2-methylpropionitrile) is suitable for moderate temperatures and well known. In the past, the chemical and free radical reactions of 2,2'-Azobis(2-methylpropionitrile) have been studied. However, the kinetic model and reaction mechanism of initiators under process conditions are still lacking. The thermal hazard characteristics evaluated by process situation of 2,2'-Azobis(2-methylpropionitrile) were discussed in this study. The kinetics analysis on AIBN is based on detailed information including rate constants, reaction orders and activation energies of the decomposition reaction. Simulated heat exchange patterns of initiators between bulk packaging and the environment can be used to collect

relevant heat hazard parameters. The results of the analysis are directly related to the storage and transportation safety of the 2,2'-Azobis(2-methylpropionitrile). Finally, a series of evaluation models about the thermal safety of initiators are constructed and analyzed by simulating the runaway modes of the 2,2'-Azobis(2-methylpropionitrile) at different temperatures.

27. **Jun Zhang a , Shun-Yao Wang a , Ying-Ying Ma b , Li-Ping Chen a , Wang-Hua Chen, Investigation of the decomposition kinetics and thermal hazards of 2,4-Dinitrotoluene on simulation approach, *Thermochimica Acta* 684 (2020), <https://doi.org/10.1016/j.tca.2019.178350>**

#### **Abstract.**

As a major intermediate in the synthesis of explosives, the destructive nature and thermal hazards of 2,4-DNT are enormous. To evaluate the potential thermal hazards for its decomposition, the differential scanning calorimeter (DSC) experiments under non-isothermal and isothermal conditions were performed to determine the decomposition kinetic model and parameters. According to the dynamic DSC results, 2,4-DNT underwent a melting process before thermal decomposition, the endothermic peak and exothermic peak are identified at about 67–70 °C and 245–272 °C, respectively. Combined with the results of non-isothermal and isothermal tests, the proper decomposition kinetic model of 2,4-DNT consists of two consecutive reactions has been created and verified. Thermal behaviors under different scenarios and thermal explosion have been simulated separately to predict the thermal hazard parameters. It can also be concluded from the simulation under external fire exposure scenario, with increasing of the filling ratios for sample, the induction period of the exothermic decomposition reaction is also continuously shortened, accompanied by greater danger.

28. **Shang-Hao Liu, Yan-Ru Wang, Chen-Rui Cao & Yen-Chun Cheng, Systematic process hazard assessment of three kinds of solid organic peroxides with kinetic analysis and heat transfer equilibrium, *Journal of Thermal Analysis and Calorimetry* (May 2020); DOI: 10.1007/s10973-020-09732-6**

#### **Abstract.**

Organic peroxide (OP) has been applied in the industry for at least 40 years. Driven by significant investments in today's high-profile energy, petrochemical, and polymer industries, the market and applications of OPs are expanding rapidly. However, the self-reactive nature has led to continuous research work on this topic. Nevertheless, tremendous progress has been made in hazard analysis, which has improved existing protocols or led to the discovery of new safety methods. OPs still cause related chemical hazards, and the limitations related to process hazards remain to be resolved. There is a lack of comprehensive systematic analysis of the process hazards of a wide variety of OPs. Different OPs, namely BPO, LPO, and the emerging OP, HTP-65W, were selected for investigation with several calorimetry techniques based on thermokinetic and heat transfer models. Determination methods have a crucial role in an operator for obtaining a systematic understanding of hazard properties under different process conditions, which is related to avoiding the occurrence of process disasters. For example, LPO has a shorter TMRad and TCL (< 1 min) than BPO and HTP-65W, indicating that LPO can be classified as an obvious hazardous material. Moreover, SADT < 25 °C can be used for evaluating LPO's cooling system efficiency.