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 arboreaby 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. *V. Leroy, D. Cancellieri, E. Leoni, Thermal degradation of ligno-cellulosic fuels: DSC and TGA studies, Thermochimica Acta, V. 451, Issues 1–2, Pages 131-138, https://doi.org/10.1016/j.tca.2006.09.017.*

Abstract

The scope of this work was to show the utility of thermal analysis and calorimetric experiments to study the thermal oxidative degradation of Mediterranean scrubs. We investigated the thermal degradation of four species; DSC and TGA were used under air sweeping to record oxidative reactions in dynamic conditions.

Heat released and mass loss are important data to be measured for wildland fires modelling purpose and fire hazard studies on ligno-cellulosic fuels. Around 638 and 778K, two dominating and overlapped exothermic peaks were recorded in DSC and individualized using a experimental and numerical separation. This stage allowed obtaining the enthalpy variation of each exothermic phenomenon. As an application, we propose to classify the fuels according to the heat released and the rate constant of each reaction. TGA experiments showed under air two successive mass loss around 638 and 778K. Both techniques are useful in order to measure ignitability, combustibility and sustainability of forest fuels.

Keywords: Wildland fire; Thermal degradation; Oxidation; Forest fuels; Ignitability; Combustibility

5. *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 H2SO4 or NaOH by DSC and VSP 2, J Therm Anal Calorim , Vol. 83 (2006) 1, 57–62*

Abstract

In this study, a mixture of methyl ethyl ketone peroxide (MEKPO) with various contaminants, such as H_2SO_4 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.

6. *S. Fischer, G. Krahn, B. Reimer, Evaluation of microcalorimetric measurements in terms of information content for decomposition reactions, Thermochimica Acta, V 445, Issue 2, (2006), 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.

7. *K. W. Wu, H. Y. Hou, C. M. Shu, Thermal phenomena studies for dicumyl peroxide at various concentrations by DSC, J Therm Anal Calorim , 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/mo1, frequency factor $k0$ is $3.124 \cdot 10^{12}$ 1/s, reaction order n is 0.9 and heat of decomposition ΔH is 750.52 J/g for DCPO 99 mass%.

8. *Ch. Zhang, Thermal decomposition study of hydroxylamine nitrate during storage and handling, master thesis, 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 ivdetermine 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.

9. *П.А.Амеличев, В.Н. Герман, С.Э.Гребенникова, А.А.Старостина, Л.В.Фомичева, Верификация формально-кинетической модели термического разложения гексогена. // Труды международной конференции IX Харитоновские тематические научные чтения «Экстремальные состояния вещества. Детонация. Ударные волны». 2007 г. Саров. Россия. 2007 – с. 169 – 178.*
(P. Amelichev, V. German, S. Grebenikova. A. Starostina, L. Fomicheva, Verification of formal kinetic model of thermal decomposition of RDX // Proceedings of IX "Chariton scientific readings Extreme states of a substance. Detonation, Shock waves", 2007, Sarov, R - p. 169 - 178)

10. *А.А. Старостина, П.А. Амеличев. Построение формальной кинетической модели термораспада октогена с целью использования её в математической модели теплового взрыва // Сборник докладов VII научно-технической конференции «Молодежь в науке». 28 – 30 октября 2008 – С. 276 – 281.* *(A. Starostina, P. Amelichev, Creation of the formal kinetic model of thermal decomposition of HMX for its application in mathematical model of thermal explosion // Proceedings of VII conference "Youth in Science", 200 - p. 276 - 281)*

11. *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 isoperobolic tests and the simulation results of the ADT24. The results are tabled hereunder.

12. *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.

13. *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 thermogravimetic 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.

14. *K-Y. Chen, S-H. Wu, Y-W. Wang, and C-M. Shu, Runaway reaction and thermal hazards simulation of cumene hydroperoxide by DSC, J. of Loss Prev 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 (?Hd) and exothermic onset temperature (T0) 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.

15. *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, J Therm Anal Calorim , 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 (dH) 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.

16. *А.А.Старостина, П.А.Амеличев, В.Н.Герман, С.Э.Гребенникова, С.А.Вахмистров. Расчетно-экспериментальный подход определения закономерностей термического разложения пластифицированного октогена для оценки его реакционной способности в изделиях // Труды международной конференции XI Харитоновские тематические научные чтения. Саров. Россия. 2009 – с. 73 – 79. (A. Starostina, P. Amelichev, V. German, S. Grebenikova, S. Vachmistrov, Combined comutational - experimental approach for determination of patterns of thermal decomposition of plasticized HMX aimed at assessment of its reactivity in articles, // Proceedings of XI international conference "Chariton scientific readings", 2009, Sarov, RF - p. 73 - 79)*

17. *Lijun Liu, Chunyang Wei, Yuyan Guo, William J. Rogers and M. Sam Mannan, Hydroxylamine nitrate self-catalytic kinetics study with adiabatic calorimetry, J. Haz. Mat, Volume 162, Issues 2-3, 15 March (2009), Pages 1217-1222*

Abstract

Hydroxylamine nitrate (HAN) is an important member of the hydroxylamine compound family with applications that include equipment decontamination in the nuclear industry and aqueous or solid propellants. Due to its instability and autocatalytic behavior, HAN has been involved in several incidents at the Hanford and Savannah River Site (SRS) [Technical Report on Hydroxylamine Nitrate, US Department of Energy, 1998]. Much research has been conducted on HAN in different areas, such as combustion mechanism, decomposition mechanism, and runaway behavior. However, the autocatalytic decomposition behavior of HAN at runaway stage has not been fully addressed due to its highly exothermic and rapid decomposition behavior. This work is focused on extracting HAN autocatalytic kinetics and analyzing HAN critical behavior from adiabatic calorimetry measurements. A lumped autocatalytic kinetic model for HAN and associated model parameters are determined. Also the storage and handling critical conditions of diluted HAN solution without metal presence are quantified.

18. *А.А Старостина, П.А. Амеличев, В.Н.Герман, С.Э.Гребенникова, С.А.Вахмистров. Расчетно-экспериментальные модели развития самоподдерживающейся реакции в ВВ при различных температурных воздействиях // Сборник докладов IX научно-технической конференции «Молодежь в науке». 2010 – С. 29 – 35. (A. Starostina, P. Amelichev, V. German, S. Grebenikova, S. Vachmistrov, Combined computational - experimental models of self-sustaining reactions in explosives under different temperature impacts, // Proceedings of IX conference "Youth in Science", 2010 - p. 29 - 35)*

19. *А.А.Старостина, П.А.Амеличев, В.Н.Герман, и др., Расчетно-экспериментальный подход определения закономерностей термического разложения пластифицированного октогена для оценки его реакционной способности в изделиях. Сборник тезисов молодежной научно-технической конференции «Эксперимент-2010». 19 – 20 мая 2010 – С. 3.* (A. Starostina, P. Amelichev, V. German et all, Combined computational - experimental approach to determination of patterns of thermal decomposition of the plasticized HMX aimed at assessment of its reactivity in articles // Proceedings of the Scientific conference "Experiment-2010", 2010 - p.31)

20. *Амеличев А.А., Старостина А.А, Гребенникова С.Э., Герман В.Н. Испытательный стенд и методика исследования теплового взрыва ВВ // Сборник докладов Русско-Китайский семинара «Эксплуатационные характеристики и свойства взрывчатых веществ» КНР. г. Мяньян. 2010 – С. 163 – 170.* (P. Amelichev, A. Starostina, S. Grebenikova, V. German, Test bench and EM cook-off investigation technique, // Proceedings of Russian-Chinese seminar "Performance characteristics and properties of explosives", 2010, Mianyang, China - p. 163 - 170)

21. *Амеличев А.А., Старостина А.А, Гребенникова С.Э., Герман В.Н. Вахмистров С.А. Расчетно-экспериментальные модели развития взрывной реакции в ВВ при различных температурных воздействиях // Сборник докладов Русско-Китайский семинара «Эксплуатационные характеристики и свойства взрывчатых веществ» КНР. г. Мяньян. 2010 – С. 131 - 137* (P. Amelichev, A. Starostina, S. Grebenikova, V. German, S. Vahmistrov, Calculation and experimental models of EM runaway reaction evolution under various thermal effects // Proceedings of Russian-Chinese seminar "Performance characteristics and properties of explosives", 2010, Mianyang, China - p. 131 - 137)

22. *Старостина А.А., Амеличев П.А., Герман В.Н., Гребенникова С.Э., Вахмистров С.А. Расчетно-экспериментальные модели развития самоподдерживающейся реакции в ВВ при различных температурных воздействиях. Труды международной конференции XIII Харитоновские тематические научные чтения. Саров. Россия. 2011 – с. 97 – 102.* (A. Starostina, P. Amelichev, V. German, S. Grebenikova, S. Vachmistrov, Combined computational - experimental models of self-sustaining reactions in explosives under different temperature impacts // Proceedings of XIII international conference "Chariton scientific readings", 2011, Sarov, RF - p. 97 - 102)

23. *А.А.Старостина, П.А.Амеличев, В.Н.Герман, С.Э. Гребенникова, С.А.Вахмистров. Расчетно-экспериментальные модели развития самоподдерживающейся реакции в ВВ при различных температурных воздействиях // Материалы конференции «Современные проблемы технической химии». Казань. 2011 – С. 171 – 179.* (A. Starostina, P. Amelichev, V. German, S. Grebenikova, S. Vachmistrov, Combined computational - experimental models of self-sustaining reactions in explosives under different temperature impacts // Proceedings of the conference "Modern problems of applied chemistry", 2011, Kasan, RF - p. 171 -179)

24. *Tseng, JM., Hsieh, TF., Chang, YM. et al. Prediction of thermal hazard of liquid organic peroxides by non-isothermal and isothermal kinetic model of DSC tests. J Therm Anal Calorim 109, 1095–1103 (2012). https://doi.org/10.1007/s10973-011-2125-1*

Abstract

Liquid organic peroxides (LOPs) have been widely used as initiators of polymerization, hardening, or cross-linking agents. We evaluated a beneficial kinetic model to acquire accurate thermokinetic parameters to help preventing runaway reactions, fires or explosions in the process environment. Differential scanning calorimetry was used to assess the kinetic parameters, such as kinetic model, reaction order, heat of reaction (ΔH_d), activation energy (E_a), frequency factor ($\ln k_0$), etc. The non-isothermal and isothermal kinetic models were compared to determine the validity of the kinetic model, and then applied to the thermal hazard assessment of commercial package contaminated with LOPs. Simulations of a 0.5-L Dewar vessel and 25-kg commercial package were performed. We focused on the thermal stability of different liquid system properties for LOPs. From the results, the optimal conditions were determined for avoiding violent heat effects that can cause a runaway reaction in storage, transportation, and manufacturing.

25. *Lung-Chang Tsai, Yun-Ting Tsai, Chun-Ping Lin, Shang-Hao Liu, Tsung-Chih Wu, Chi-Min Shu, Isothermal versus non-isothermal calorimetric technique to evaluate thermokinetic parameters and thermal hazard of tert-butyl peroxy-2-ethyl hexanoate, J Therm Anal Calorim (2012) 109:1291–1296, DOI 10.1007/s10973-012-2519-8*

Abstract

Liquid organic peroxides have been broadly employed in the process industries such as tert-butyl peroxy-2-ethyl hexanoate (TBPO). This study investigated the thermokinetic parameters of TBPO, a typical liquid organic peroxide, by isothermal kinetic algorithms and non-isothermal kinetic algorithms with thermal activity monitor III, and differential scanning calorimetry, respectively. An attempt has been made to determine the thermokinetic parameters by simulation software, such as exothermic onset temperature (T_0), maximum temperature (T_{max}), decomposition (ΔH_d), activation energy (E_a), self-accelerating decomposition temperature, and isothermal time to maximum rate (TMR_{iso}). A liquid thermal explosion model was established for a reactor containing liquid organic peroxide of interest. From experimental results, liquid organic peroxides' optimal conditions for avoiding a violent runaway reaction of storage and transportation were created.

26. *A.Yu. Snegirev, V.A. Talalov, V.V., Stepanov, J.N. Harris, Formal kinetics of polystyrene pyrolysis in non-oxidizing atmosphere, Thermochimica 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, the kinetic parameters were derived by means of the isoconversional method, the peak value method, the Kissinger method, 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 nth 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 nth 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.

27. *А.А.Старостина, П.А.Амеличев, В.Н.Герман, С.Э.Гребенникова, Л.В. Фомичева. Кинетическая модель термического разложения ВВ, учитывающая влияние степени заполнения реакционного объёма // Труды международной конференции XV Харитоновские тематические научные чтения. Саров. Россия. 2013 – с. 219 – 227. (A. Starostina, P. Amelichev, V. German, S. Grebenikova, L. Fomicheva, Kinetic model of thermal decomposition of an explosive which takes into account effect of filling ratio of the reactive vessel // // Proceedings of XV international conference "Chariton scientific readings", 2013, Sarov, RF - p. 219 - 227)*

28. *V. Leroy-Cancellieri, D. Cancellieri, E. Leoni et al. A global mechanism for the thermal degradation of peat, Proceedings of 4th Fire Behavior and Fuels Conference, July 1-4, 2013, St. Petersburg, Russia, Published by the International Association of Wildland Fire, Missoula, Montana, USA*

Abstract.

Investigations were performed in order to improve the energetic characterization of peats with different geological origin, hydrology, and botanical composition. Special attention was focused on the effects of thermal treatment of peat degradation in oxidative atmosphere and its kinetics. Experiments were carried out by thermogravimetry. Starting with dehydration step between 300 and 423K, the main thermal decomposition process under air showed two distinct degradation zones, corresponding to devolatilisation step between 473 and 650K and combustion step between 650 and 773K. Based on the experimental results, the kinetic parameters for boreal peats pyrolysis and combustion reactions were calculated using a three-steps model. The kinetic triplet of each reaction was calculated using Hybrid Kinetic Method. Our results show a good correlation between experiments and simulations with a three-step model.

29. *Leroy-Cancellieri, V., Cancellieri, D., Leoni, E. et al. Energetic potential and kinetic behavior of peats. J Therm Anal Calorim v. 117, pp. 1497–1508 (2014). https://doi.org/10.1007/s10973-014-3912-2*

Abstract.

Investigations were conducted with the aim to improve the energetic characterization of peats with different geological origin, hydrology, and botanical composition. Special attention was paid to the effects and kinetics of thermal treatment of peat decomposition in an oxidative atmosphere. Experiments were carried out using thermogravimetry, differential scanning calorimetry, and a calorimetric bomb. The present study shows that thermal decomposition process consists in a devolatilization step between 473 and 650 K and a combustion step between 650 and 773 K. Thermochemical properties (i.e., degree of decomposition, ultimate analysis, and heating value) were determined for each sample and correlated to thermal behavior. Based on the experimental results, the kinetic parameters for pyrolysis and combustion of boreal peat were estimated using a three-step model. The kinetic triplet of each reaction was estimated using the hybrid kinetic method Cancellieri et al. (Thermochim Acta 438:41–50, 2005). These results will assist in the development of an energetic classification of peat fuels.

30. *K.-H. Hsueh, W-C. Chen, W-T. Chen, C-M. Shu, Thermal decomposition analysis of 1,1-bis(tert-butylperoxy)cyclohexane with sulfuric acid contaminants. J. of Loss Prevention in the Process Industries, 40 (2016) 357-364.*

Abstract.

Owing to the thermally unstable 1,1-bis(tert-butylperoxy)cyclohexane (BTBPC) having two active OeO 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 (To), peak temperature (Tp), apparent activation energy (Ea), heat of decomposition (D Hd), 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. H2SO4 appears to inhibit the decomposition reaction of BTBPC, especially when BTBPC is mixed with 8.0 N H2SO4.

31. **S. H. Duerrstein, C. Kappler, I. Neuhaus, M. Malow, M. Schulz, M. 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 calorimetry, 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.

32. **П.С.Белухина, В.А.Бурнашов, С.А.Вахмистров, С.Э. Гребенникова, Н.А.Мирошниченко,**
Ю.В.Шейков. Влияние размерных эффектов и структуры гексогена на его реакционную
способность. // Труды международной конференции XIX Харитоновские тематические научные
чтения. Саров. Россия. 2017 – с. 138 – 147. (P. Beluchina, V. Burnashov, S. Vachmistrov, S. Grebennikova, N. Miroshnichenko, Yu. Sheikov, Effects of size factors and structure of RDX on its reactivity. // Proceedings of XIX international conference "Chariton scientific readings", 2017, Sarov, RF - p. 138 - 147)

33. **S-Y. Wang, A. A. Kossoy, Y-D. Yao, L-P. Chen, W-H. 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.

34. **Z. Dong, L-P. Chen, Y-Y. Ma, H-I. Peng, W-H.a 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.

35. **Y-F. Cheng, S-H. Liu, C-M. Shu, B. Zhang, Y-F. 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.

36. *Tsai, SY., Lin, HY., Hong, WP. et al. Evaluation of preliminary causes for vitamin D series degradation via DSC and HPLC analyses. J Therm Anal Calorim 130, 1357–1369 (2017). https://doi.org/10.1007/s10973-017-6209-4*

Abstract

Scientific evidence suggests that 25-(OH) vitamin D serum levels should be above 75 nmol L?1, which is the level required for the beneficial effects of vitamin D on long-latency diseases. Supplementing vitamin D in a daily diet is advantageous for the health of elderly individuals. The focus of this study was on the causes of vitamin D2 and D3 degradation, such as vitamin D2 being left in the open for days. The differences in the analysis results for fresh vitamin D and vitamin D stored in air for several days were compared. Comparisons were also made of the differences in vitamins D2 and D3 and their origins, i.e., oxidation, thermal decomposition, and photolysis, using high-performance liquid chromatography analyses and differential scanning calorimetry tests. We also developed a novel approach to examine the effect of heat on vitamin D, including the heat reactivity properties of vitamins D2 and D3, such as the kinetics of endothermic and exothermic reactions, the natural logarithm of the pre-exponential factor (lnk 0), reaction order (n), activation energy (E a), enthalpy of melting (?H), heat of decomposition (?H d), isothermal conditions for the time to maximum rate, total energy release, and time until 10% conversion limited. Overall, the parameters, the reactivity properties, and the degradation results can be applied to determine the optimal conditions for vitamins D2 and D3 during cooking, storage, heat treatment, and food processing that will be beneficial to human health.

37. *Lee, MH., You, ML., Laiwang, B. et al. Isothermal and non-isothermal calorimetric techniques combined with a simulation approach for studying the decomposition characteristics of di(2,4-dichlorobenzoyl) peroxide. J Therm Anal Calorim 127, 1099–1106 (2017). https://doi.org/10.1007/s10973-016-5973-x*

Abstract

Disasters caused by organic peroxides, such as di(2,4-dichlorobenzoyl) peroxide (DCBP), are mainly attributed to the presence of unstable oxygen atom bonds. In this study, DCBP was investigated through differential scanning calorimetry and thermal activity monitor III, which yielded thermokinetic data to delve into the pure decomposition characteristics of DCBP undergoing chemical reactions. In addition, the thermokinetic data were used to determine the thermal safety parameters through simulation using a best-fit approach based on an appropriately chosen kinetic model and thermal safety software. We found that DCBP decomposes more satisfactorily by an autocatalytic reaction at low temperatures. The apparent activation energy determined through various approaches, such as Kissinger and Ozawa methods, and thermal safety software simulation were studied. Although DCBP decomposition deposits with dioxins, which require major decontamination measures, DCBP is used to produce silicone products globally. The present study establishes threshold thermokinetic parameters for packing and handling thermally sensitive organic peroxides; these thresholds help predict unwarranted runaway reactions, which entail enormous pressure rise and release of toxic by-products to the environment.

Keywords: Di(2,4-dichlorobenzoyl) peroxide (DCBP), DSC, Thermal activity monitor III, Apparent activation energy, Thermal safety software

38. *R. Wei, S. Huang, Z W., R. Yuen, J. Wang, Evaluation of the critical safety temperature of nitrocellulose in different forms, J. 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 Kissiger–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.

39. *R-C. Wei, S-S. Huang, Z. Wang, Y. He, R. Yuen, J. 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, Kissiger - 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.

40. *Xiao-Yu Gan, Sen Yang, Shun-Yao Wang, Xin-Yi Guo, Li-Ping Chen, Wang-Hua Chen, Thermal behavior of benzoyl peroxide mixed with NaOH solution, Thermochimica Acta, Volume 670, 2018, P. 13-17, https://doi.org/10.1016/j.tca.2018.10.003.*

Abstract:

In order to research thermal behavior of benzoyl peroxide(BPO) mixed with NaOH solution, dynamic and isothermal experiments were carried out by differential scanning calorimeter (DSC).Thermal safety software (TSS) was used to analysis thermal behavior. Two methods were established to obtain reaction thermodynamic parameters, model-free method(Friedman method) and model-based method. By Friedman method, the activation energy of BPO with NaOH solution changed greatly, which demonstrated that the reaction was a multi-step reaction. By model-based method, BPO with NaOH solution can be described as A→B→C, where the first step A→B is an autocatalytic reaction, the second step B→C is a n-order reaction. Finally, the self-accelerating decomposition temperature(SADT) was predicted and the result indicated that SADT of BPO with NaOH solution is -1℃, which is much lower than BPO.

Keywords: BPO with NaOH solution; DSC; Thermal safety software(TSS); Thermal stability

41. *П.С.Белухина, С.А.Вахмистров, С.Э. Гребенникова, Н.А.Мирошниченко, Д.А.Кащеев, А.А.Старостина, Ю.В.Шейков, Кинетическая модель термического жидкофазного разложения пластифицированного тэна. // Труды международной конференции XXI Харитоновские тематические научные чтения. Саров. Россия. 2019 – с. 53 – 61. (P. Beluchina, S. Vachmistrov, S. Grebennikova, N. Miroshnichenko, D. Kaschev, A. Starostina, Yu. Sheikov, Kinetic model of thermal decomposition of plasticized PETN in liquid-phase // Proceedings of XXI international conference "Chariton scientific readings", 2019, Sarov, RF - p. 53 - 61)*

42. *L. Zhao, Y. Yin, H. Sui, Q. Yu, S. Sun, H. Zhang, S. Wang, L. Chen, J. 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.

43. *H-B. Li, S-Y. Wang, X-Y. Gan, W-H. Chen, L-P. Chen, Thermal risk analysis of benzoyl peroxide in the presence of phenol: Based on the experimental and simulation approach, Thermochimica Acta, V 681, (2019) https://doi.org/10.1016/j.tca.2019.178354*

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.

44. *C. Li, F. Ma, J. Sun, H. Sui, Q. Yu , L. Zhao, Y. Yin, Thermal hazard evaluation of N-guanylurea dinitramide (GUDN) by using kinetic-based simulation approach, J Therm Anal Calorim , (2019) https://doi.org/10.1007/s10973-019-09074-y*

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 $da/dt=2.29*1023exp(-225.24/R/T)(1-a)^{1.76}(a^{1.47}+0.59exp(-18.3/R/T))$. The reaction model exhibits a reasonable fitting to the experimental results with a high correlation coefficient $R2$ 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.

45. *Dong, Z., Xue, BB., Chen, Lp. et al. A study of classifying autocatalytic strength with adiabatic conditions. J. Therm Anal Calorim 137, 217–227 (2019). https://doi.org/10.1007/s10973-018-7892-5*

Abstract

Autocatalytic decompositions are common in fine chemistry. They are considered hazardous because they give rise to sudden heat evolution, often with unexpected initiation and unknown exogenous influences. The expression of autocatalytic factor Z cited from Benito-Perez model was firstly introduced. Through thermal safety software, simulations with different autocatalytic factors were carried out. The results demonstrated that the increase in autocatalytic factor resulted in the stronger autocatalytic decomposition. Furthermore, by the normalization of simulation curves, the relationship between autocatalytic strength and curve shape was found, i.e., higher degree of autocatalysis produced more meandering curve. The standard curves with different levels of autocatalytic factors were determined next. According to the standard curves area, five zones for different strengths of autocatalysis were divided, i.e., weak or no autocatalysis, less weak autocatalysis, moderate autocatalysis, less strong autocatalysis and strong autocatalysis. Finally, this classification approach was applied to two well-known substances, dicumyl peroxide and dimethyl sulfoxide; the rationality of this approach was verified by comparing classification results with previous studies. From this research, a new approach (normalization contrast method) is proposed to conveniently identify the autocatalytic strength for adiabatic instruments.

46. *Chen-Rui Cao, Shang-Hao Liu, Thermal hazard characteristic evaluation of two low-temperature-reactive azo compounds under adiabatic process conditions, Proc. Saf. Env.I Prot. V. 130, (2019), P. 231-237; https://doi.org/10.1016/j.psep.2019.08.020*

Abstract

As a key initiator of polymerization, azo compounds (azos) can supply abundant energy to the polymerization process. Although polymerization can be implemented more smoothly and the product can be modified, the use of azos also increases the probability of process hazards caused by high heat accumulation and release. To preserve the thermal safety of using azo initiators in the synthesis process, the frequently used azo initiators dimethyl 2,2?-azobis(2-methyl propionate) (AIBME) and 2,2?-azobis(2,4-dimethylvaleronitrile) (ABVN) were chosen for investigation. Under process conditions, initiators are essential for evolving and monitoring chemical reactions on both the laboratory scale and process environment. The assessment, control, and mitigation of reaction hazards are primarily based on kinetic models, which are used to estimate multiple critical safety parameters, such as TMRad in process safety and TCL and SADT in storage and transportation operation. The data from the adiabatic calorimeter correspond to real process situations are combined with the nonlinear adiabatic kinetic model, which is rarely applied to analyze the thermal hazard properties of azos. The results indicated that the kinetic model of azos in the actual process, the thermal hazard characteristics, and simulation of the runaway mode of azos in setting boundary conditions should also be investigated.

47. *Sharikov I.V., Sharikiv F.I., Identifying Safe Operating Conditions for Chemical Reactors and Storage Facilities for Potentially Hazardous Chemical Products, Eng Technol Open Acc, (2019), p. 60, DOI: 10.19080/ETOAJ.2019.03.555609*

Abstract

In the Article the main sources of danger in the operation of technological equipment are considered. The main sources of hazards have been identified - this is the problem of the emergence and development of a thermal explosion during the operation of technological equipment and storage facilities. The basic conditions for the analysis of the occurrence and development of a thermal explosion are derived based on an analysis of the equations of thermal and material balance in reactors and other equipment, where exothermic reactions can occur.

Equations are obtained for a different mechanism of heat energy transfer, due to conduction, and convection, both forced and natural. The basics of numerical methods for solving the corresponding equations in partial derivatives are considered.

48. *П.С.Белухина, С.А.Вахмистров, С.Э. Гребенникова, Н.А.Мирошниченко, А.А.Старостина, Ю.В.Шейков. Кинетическая модель термического разложения пластифицированного ВВ БТФ. Труды международной конференции XXI Харитоновские тематические научные чтения. Саров. Россия. 2019 – с. 180 – 187.* (P. Beluchina, S. Vachmistrov, S. Grebennikova, N. Miroshnichenko, A. Starostina, Yu. Sheikov, Kinetic model of thermal decomposition of plasticized BTF // Proceedings of XXI international conference "Chariton scientific readings", 2019, Sarov, RF - p. 180 - 187)

49. *S.H. Liu, Y.M. Lu, C. Su, Thermal hazard investigation and hazardous scenarios identification using thermal analysis coupled with numerical simulation for 2-(1-cyano-1-methylethyl) azocarboxamide, J. Hazard. Mater. (2020), V. 384, https://doi.org/10.1016/j.jhazmat.2019.121427*

Abstract

Polymers are salient participants in the current world, and roughly more than 40%–45% of all industrial polymers were produced by free radical polymerization. Azo-initiators now have been the foremost radical initiator with the virtue of low tendency to undergo chain transfer reactions. Nevertheless, azo-initiators are readily to decompose and release an immense amount of heats and gases under elevated ambient temperature. 2-(1-Cyano-1-methylethyl)azocarboxamide (CABN) was deliberately picked as an example for identifying the hazardous scenarios in the application of azo-initiators. Initially, thermal analysis technologies were used to investigate the thermal decomposition characteristics of CABN, and selected decomposition mechanism functions were verified for the best-fitting thermokinetic model. Subsequently, thermokinetic-based numerical simulations were implemented to evaluate the thermal hazards of CABN under the ideal adiabatic scenario. Process safety parameters under adiabatic conditions including time to maximum rate as well as induction period were consequently retrieved. Furthermore, inherent safety recommendations for free-radical polymerization were established to forestall the process accidents in storage and the applications of azo-initiator.

50. *Shang-Hao Liu, Bin Zhang, Chen-Rui Cao, Assessing the thermal properties of [Bmim]NO3 through thermokinetic calculations and the energy equilibrium method, Process Safety and Environmental Protection, Volume 134, (2020), Pages 270-276 https://doi.org/10.1016/j.psep.2019.12.007Get rights and content*

Abstract

Using batteries to convert chemical energy into electrical energy is one of the significant technologies that must be enhanced in the 21 st century. In the fuel battery development area, ionic liquids (ILs) are outstanding electrolytes for batteries. According to their thermophysical and phase equilibrium properties, ILs are widely used in different energy fields due to their diversity in the synthesis field. However, there are few detailed thermokinetic studies on ILs. To ensure the thermal safety of ILs in the process of creation, a commonly used IL, 1-butyl-3-methylimidazolium nitrate ([Bmim]NO3), was chosen for exploration. In this study, thermal decomposition characteristics were obtained by differential scanning calorimetry. The obtained data were input into the thermokinetic equation to determine the basic thermal hazards of [Bmim]NO3. In addition, based on thermal equilibrium theoretical models, the reaction kinetics and critical safety parameters were extrapolated for consideration. The influences of the sample mass and the overall heat transfer coefficient were simulated and discussed in 25.0 g and 50.0 g packages. The results showed that [Bmim]NO3 had a shorter TMRad and TCL (<1 day) when the temperature was greater than 200 °C. Moreover, SADT<150 °C can be used for evaluating the cooling system efficiency of [Bmim]NO3.

51. *S-H. Liu, C-R. Cao, W-C. Lin, C-M. Shu, Experimental and numerical simulation study of the thermal hazards of four azo compounds, J. 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 ca lorimetry 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.

52. *H-B. Li, W-G. Wu, X. Peng, X. Wang, X-Y. Guo, L. Chen, W-H. Chen, Research on the decomposition kinetics and thermal hazards of 2,2'-azobis(2-methylpropionamidine) dihydrochloride by experimental and simulation approach, Thermochimica Acta (to be published)*

Abstract.

The thermal behaviors of azo-compounds have been a topic received extensive attention. This paper attempted to obtain the decomposition kinetics of 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) by applying differential scanning calorimeter (DSC) experiments and slow cook-off test. Moreover, the thermal hazards parameters, such as self-accelerating decomposition temperature (SADT), time to maximum rate under adiabatic conditions (TMR ad), time to conversion limit (TCL), were predicted.

The results indicate that AIBA is a highly exothermic and hazardous substance, and the kinetic model including two-step parallel reaction paths, the n-order reaction and the autocatalytic reaction, is credible to evaluate the decomposition process of AIBA. Based on the kinetic model and fiberboard packaging, the simulated SADT of 50 kg drum and 25 kg box are 94 °C and 91 °C, respectively. The TMR ad is 104.66 °C under 24 h, and 113.05 °C of 8 h.

53. *F. Yang, Y. Chen, C. Zhao and L. Zhang, Studies on the thermal behavior and safety of a novel thermostable explosive BPTAP, Royal Society of Chemistry: RSC Adv.,2019,9, 22198, DOI: 10.1039/c9ra03385h*

Abstract.

Thermal decomposition of a highly thermostable explosive dihydroxylammonium 2,4,8,10-tetranitro-benzopyrido-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, thermo-analytical 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.

54. *C-R. Cao, S-H. Liu, J-H. Chi, C-M. Shu, Using thermal analysis and kinetics calculation method to assess the thermal stability of azobisdimethylvaleronitrile, J Therm Anal Calorim (2019), 138, (1) DOI: 10.1007/s10973-019-08385-4*

Abstract.

Azo compounds used in catalytic reactions often exhibit self-reactivity and high exothermicity. Severe fires and explosions can occur if the stage of change in the reaction (e.g., in an endothermic process or cooling system) is weaker than in a fractional heat release process. To guarantee the thermal safety of azo initiator in the production process, azobisdimethylvaleronitrile (ABVN), a normally applied azo in polymerization, was selected for the study. The basic thermal hazards of ABVN were obtained by simulating the exothermic curves of ABVN with differential scanning calorimetry technique, and the self-accelerating decomposition temperature (SADT) was calculated by combining the kinetics of the reaction. Analyzing the impact of different packaging conditions on SADT, values were verified with simulation methods performed with the packaging of 25.0 kg and 50.0 kg of ABVN. The results showed that the SADT was lower than 50 °C. Therefore, it is essential to establish a style of computing that can more rapidly determine the value of SADT, avoiding time-consuming and costly large-scale experiments.

55. *Cao, C., Shu, C. Kinetic modeling for thermal hazard of 2,2'-azobis (2-methylpropionamide) dihydrochloride using calorimetric approach and simulation. J Therm Anal Calorim 137, 1021–1030 (2019) doi:10.1007/s10973-018-07995-8*

Abstract.

Azo compounds are usually used as initiators and blowing agents. They are also typically self-reactive materials capable of undergoing a runaway reaction during storage or transportation, which can cause serious fires and explosions. To prevent the thermal hazard of azos occurring in a real process, transportation, or storage, azo initiator 2,2'-azobis (2-methylpropionamide) dihydrochloride (AIBA), which has few studies on relevant research in thermal safety, was selected to be investigated. First, the features of thermal decomposition under non-isothermal condition of AIBA were attained through differential scanning calorimetry and simultaneous thermal analysis. Second, the collected data were substituted into mathematical analyzer to evaluate the basic thermal hazard for AIBA. In addition, based on Semenov theoretical model and thermokinetic parameters, the critical ignition temperature (TCI) was extrapolated for consideration of surroundings temperature under specific cooling system (TS). The results provided process control data and the consequences of thermal runaway for AIBA. In addition, the related numerical methods for prevention of thermal runaway reaction could be calculated during process deviation. Therefore, the assessment conclusions also showed that process parameters must be measured and controlled strictly to generate the desired reaction. The results showed that the various TCI were all less than 70 °C. Therefore, it is essential to avoid a temperature beyond the TCI or cooling system failure.

56. *Cao, CR., Liu, SH., Chi, JH. et al. Using thermal analysis and kinetics calculation method to assess the thermal stability of azobisdimethylvaleronitrile*
J Therm Anal Calorim (2019) 138: 2853-2863. https://doi.org/10.1007/s10973-019-08385-

Abstract.

Azo compounds used in catalytic reactions often exhibit self-reactivity and high exothermicity. Severe fires and explosions can occur if the stage of change in the reaction (e.g., in an endothermic process or cooling system) is weaker than in a fractional heat release process. To guarantee the thermal safety of azo initiator in the production process, azobisdimethylvaleronitrile (ABVN), a normally applied azo in polymerization, was selected for the study. The basic thermal hazards of ABVN were obtained by simulating the exothermic curves of ABVN with differential scanning calorimetry technique, and the self-accelerating decomposition temperature (SADT) was calculated by combining the kinetics of the reaction. Analyzing the impact of different packaging conditions on SADT, values were verified with simulation methods performed with the packaging of 25.0 kg and 50.0 kg of ABVN. The results showed that the SADT was lower than 50 °C. Therefore, it is essential to establish a style of computing that can more rapidly determine the value of SADT, avoiding time-consuming and costly large-scale experiments.

57. *A-D. Yu, C-R. Cao, X-H. Pan, C-M. Shu, W-J. Wang, Solid thermal explosion of autocatalytic material based on nonisothermal experiments: Multistage evaluations for 2,2'-azobis(2-methylpropionitrile) and 1,1'-azobis(cyclohexanecarbonitrile) Process Safety Progress, V38, Issue4, 2019, https://doi.org/10.1002/prs.12058*

Abstract.

To achieve the thermal stability characteristics of azo compounds, a method for characterizing the kinetics of the reaction and decomposition for azo compounds based on nonisothermal calorimetric data was explored. Differential scanning calorimetry (DSC) was employed to analyze the thermal decomposition of two azo compounds, 2,2′-azobis(2-methylpropionitrile) and 1,1′-azobis(cyclohexanecarbonitrile). DSC experiments were performed to acquire the exothermic peak temperature (Tp), exothermic final temperature (Tf), and heat of decomposition ($\triangle$Hd). Corresponding thermokinetics were calculated using Flynn-Wall-Ozawa method. Moreover, data determined through DSC experiments were utilized to predict the self-accelerating decomposition temperature, control temperature, and emergency temperature. A nonisothermal experiment was performed to investigate the runaway characteristics of azo compounds, the melting behavior that occurred in the decomposition process interfered with thermal analysis. Through dividing the reaction into several stages, multistage evaluations were carried out in the process of our study. During the thermal explosion simulation, the actual packing parameter of 25.0 kg was applied to ensure that the simulation results were more practical. Thermal safety parameters acquired from the simulation results can provide information on loss prevention and facilitated the establishment of an emergency relief system.

58. *Vikranth Volli, Wei-Cheng Lin, Gubbala Vinay Sai Krishna, Harsh Bhardwaj, Chi-Min Shu, Oxidative stability, thermal hazard analysis, and decomposition kinetics of 1-methylimidazolium nitrate via DSC, TGA, and GC/MS, J Therm Anal Calorim, 138, 3403-3413 (2019) https://doi.org/10.1007/s10973-019-08853-x*

Abstract.

Imidazolium-based ionic liquids are green solvents used as separation and electrolyte media in liquid–liquid extraction processes and electrochemical devices. However, they are volatile and flammable once they reach their thermal decomposition temperatures. In the present study, the oxidative stability, decomposition, and combustion reaction of 1-methylimidazolium nitrate [Mim][NO$_3$] were investigated via thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). TG analysis revealed a single-stage mass loss between 117.6 and 230.2 C with oxidative onset temperatures in the range of 126.6–163.2 C with the increase in heating rate (1.0, 2.0, 4.0, and 8.0 C min -1). DSC results indicated the degradation as exothermic with the average enthalpy of decomposition as 1610.4 J g -1. The estimated average value of apparent activation energy using isoconversional methods such as Kissinger, FWO, and Friedman was in the range of 106.1–114.2 kJ mol -1, and the reaction function (autocatalytic model) is expressed as: f(a) = (1 - a) 1.42 (0.017 ? a0.62) using multivariate nonlinear regression. The GC/MS analysis revealed the formation of methane isocyanate indicating the hazardous, toxic, corrosive, and carcinogenic nature of the decomposed gases. This research was aimed to develop a predictive model for oxidative degradation behavior and to provide the necessary basis for the design of precise safety systems.

59. *S-H. Liu, C-R. Cao, W-C. Lin, C-M. 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 ca lorimetry 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.

60. *Rao, G., Feng, W., Zhang, J. et al. Simulation approach to decomposition kinetics and thermal hazards of hexamethylenetetramine. J Therm Anal Calorim 135, 2447–2456 (2019). https://doi.org/10.1007/s10973-018-7359-8*

Abstract

The thermal stability of HMT under dynamic, isothermal and adiabatic conditions was investigated using differential scanning calorimeter (DSC) and accelerating rate calorimeter (ARC), respectively. It is found from the dynamic DSC results that the exothermic decomposition reaction appears immediately after endothermic peak, a coupling phenomenon of heat absorption and generation, and the endothermic peak and exothermic peak were indentified at about 277–289 and 279–296 °C (Tpeak) with the heating rates 1, 2, 4 and 8 °C min−1. The ARC results reveal that the initial decomposition temperature of HMT is about 236.55 °C, and the total gas production in decomposition process is 6.9 mol kg−1. Based on the isothermal DSC and ARC data, some kinetic parameters have been determined using thermal safety software. The simulation results show that the exothermic decomposition process of HMT can be expressed by an autocatalytic reaction mechanism. There is also a good agreement between the kinetic model and kinetic parameters simulated based on the isothermal DSC and ARC data. Thermal hazards of HMT can be evaluated by carrying out thermal explosion simulations, which were based on kinetic models (Isothermal DSC and ARC) to predict several thermal hazard indicators, such as TD24, TD8, TCL, SADT, ET and CT so that we can optimize the conditions of transportation and storage for chemical, also minimizing industrial disasters.

61. *H-B. Wu, S-H. Liu & C-R. 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.

62. *Feng-Jen Chu; Terng-Jou Wan, Chen-Rui Cao, Shang-Hao Liu; Calorimetric studies and kinetic determination of fires and explosions of a chemical processing of dicumyl peroxide J Therm Anal Calorim, (2020); DOI: 10.1007/s10973-020-09310-w*

Abstract.

The polymerization industry has existed for many years. The advancement of industrial technology is contributed to the related synthesis and application of enduring polymer operation. Organic peroxide (OP) initiators have been used and applied to practical industrial processes which may cause a runaway reaction due to their self-reactive property. OPs have been used for a long time and studied in the related literature. However, there are still emerging OPs that have recently been applied to these processes, and there are few related studies. To ensure the thermal safety of OPs in the process of production, transportation, and storage, the common OP initiator such as dicumyl peroxide (DCPO) was selected to be investigated. First, thermal decomposition characteristics under non-isothermal and adiabatic conditions of DCPO were acquired by differential scanning calorimetry. Second, combined calorimetry with pseudo-adiabatic and isothermal conditions can determine the process of thermal hazards and basic reaction patterns. The gleaned data can input into a mathematical model to evaluate the basic thermal hazards for DCPO, respectively. In addition, based on simulated thermal explosion models and kinetic parameters, hazardous properties of storage and transport can also be acquired. The results show that the DCPO has prominent hazard properties on thermal and explosive hazards in process conditions which should pay much attention to temperature during storage and transportation.

63. *Wen-qian Wu, Wei Feng, Qiu-han Lin, Shun-yao Wang, Zi-chao Guo, Li-ping Chen, Wang-hua Chen, Synthesis and thermal decomposition of TNPG; Thermoch. Acta, (January 2020), Vol. 683, 178396; DOI: https://doi.org/10.1016/j.tca.2019.178396*

Abstract.

1, 3, 5-Trihydroxy-2, 4, 6-trinitrobenzene (TNPG) is an essential energetic intermediate for synthesis of 1, 3, 5-Triamino-2, 4, 6-Trinitrobenzene (TATB). The thermal stability of TNPG was studied in this work. First, TNPG was synthesized by nitration of 1, 3, 5-trihydroxybenzene with the solution feeding. Then, the thermal stability of TNPG was studied by DSC and ARC experiments. The non-isothermal DSC results indicated that the thermal decomposition of TNPG overlapped with the endothermic melting process. The isothermal DSC and ARC results evidenced that the decomposition of TNPG followed the autocatalytic mechanism. Two different models were

constructed to depict the decomposition process of TNPG. By comparison with the isothermal DSC results, it was found that the following model could better describe the decomposition process of TNPG: A→BS (autocatalytic), A→Aliq (melting), Aliq→B (autocatalytic).

64. *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 ℃ and 245–272 ℃ , 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 separatelyto 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.

65. *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.

66. *Andong Yu, Weijun Wang, Min Hua, Xuhai Pan, Xinmiao Liang, Chenye Wei, Chi-MinShu, Juncheng Jiang, Thermal hazard analysis of 1-((cyano-1-methylethyl) azo) formamide and effect of incompatible substances on its thermal decomposition, Journal of Loss Prevention in the Process Industries, Volume 65, May 2020, 104098 https://doi.org/10.1016/j.jlp.2020.104098*

Abstract.

1-((cyano-1-methylethyl) azo) formamide (CABN) is an azo compound that exhibits high thermal sensitivity and self-reactivity. Because of incorrect operation, incompatible substances and other dangerous conditions, thermal explosion accidents may occur during the manufacturing, storage, and transportation of CABN. The pyrolysis characteristics of CABN and its mixture for various heating rates were assessed using differential scanning calorimetry. The results showed that incompatible substances increased the risk of CABN. Moreover, the thermal runaway of CABN under an adiabatic condition was studied using an adiabatic rate calorimeter to obtain the parameters under adiabatic condition. Based on the experimental data, the kinetic parameters of CABN and its mixtures were obtained. In addition, a thermal decomposition kinetic model of CABN was created using Thermal Safety Series. All experiments have shown that the conditions and parameters of CABN must be strictly controlled.

67. *Liu, SH., Wang, YR., Su, C.H. et al. Thermal hazard estimation of HTP-65W with kinetic equations and heat transfer model. J Therm Anal Calorim (Oct 2020). https://doi.org/10.1007/s10973-020-10363-0*

Abstract.

Organic peroxides (OPs) have a long history in the industry. In particular, it mainly occupies a leading position in the polymer industry, so there are still emerging substances being put into the current market and applications. However, the well-known aspect of OPs in the past is reflected in their self-reactive and hazardous properties, which have continued to expand related research in the field of safety. However, even under the rich research foundation and new safety technologies, the thermal hazards caused by emerging OPs are still heard, which means that the application of new OPs still needs attention and solutions in safety area. It is necessary to update the hazard knowledge of emerging OPs and achieve the purpose of disaster reduction. Therefore, the new OP, HTP-65W was selected for this study, starting from kinetic analysis and combining the heat transfer mode of the external system to estimate and assess the overall hazard characteristics between the material and the heat exchange of the environment. The basic experiment is carried out under the technical conditions of the isothermal calorimetric test which conformed to real situation. Evaluating the thermal hazard mode of a substance can establish the

determination of safety parameters, and it is essential to the actual operation process. If the substance can be controlled at a specific ambient temperature or the decomposition reaction can be prevented, the possible hazards can be eliminated. For example, HTP-65W has shorter TMRad and TCL, which shows that HTP-65W has obvious reactivity hazards. In addition, evaluating the thermal hazards of HTP-65W in different containers can be used as a safety basis for the design of HTP-65W's cooling system and on-site operations.

68. *Jun Zhang , Ying-Ying Ma , Li-Ping Chen, Wang-Hua Chen, Experimental and numerical simulation to identify the thermal hazards and hazardous scenarios of N-Nitrodihydroxyethyl dinitrate, Process Safety and Environmental Protection, 145, (2021), 211–221*

Abstract.

As a major high-energy plasticizer in the production of propellant, the destructive nature and thermal hazards of DINA are enormous. To evaluate the potential thermal hazards for its decomposition, the non-isothermal DSC and ARC experiments were performed to determine the decomposition kinetic model and parameters. It can be seen from the DSC results that DINA underwent a melting process before thermal decomposition, the endothermic peak and exothermic peak are identified at about $49-52{\circ}C$ and $153-162{\circ}C$, respectively. Combined with the results of DSC and ARC tests, the reliable kinetic model of DINA consists of four consecutive autocatalytic reaction has been created and verified. Subsequently, kinetic-based numerical simulations were executed to evaluate the thermal explosion hazards of DINA under the different scenarios. Process safety parameters under adiabatic conditions including time to maximum rate as well as induction period were consequently retrieved. Furthermore, inherent safety recommendations were proposed to forestall the process accidents in storage and the applications of DINA.

69. *Chia-Feng Tsai, I-Jyh Wen, Shang-Hao Liu, Chen-Rui Cao, Han Zhang, Evaluation of thermal hazard characteristics of four low temperature reactive azo compounds under isothermal conditions; J. Loss Prev. in Proc. Ind., 71,(2021), 104453, https://doi.org/10.1016/j.jlp.2021.104453*

Abstract.

- The results of laboratory-scale were used to identify thermal hazards in the plant.
- The kinetics of four azos was studied by analytical model.
- Kinetic simulations were used to evaluate of thermal equilibrium for four azos.
- The kinetic model under the process conditions is determined.
- Thermal stability (TMRad and TCL) with runaway reaction was found by analysis.

The polymerization reaction can lower the threshold of the required energy by the initiator to improve the efficiency of the overall process reaction. Emerging polymerization initiators are also a major focus of process improvement and technological progress. Azo compounds (azos), which used in dyeing applications, are subsequently used in polymerization reactions due to their highly exothermic reaction characteristics. Although higher heat release can promote polymerization and modify the product, heat generation may also cause process hazards.

These thermal hazard parameters were studied by selecting dimethyl 2,2′-azobis(2,4-dimethylvaleronitrile) (ABVN), 2,2′-azobis(2-methyl propionate) (AIBME), 2,2′-azobis(2-methylpropionamide) dihydrochloride (AIBA), and 2,2′-azobis(isobutyronitrile) (AIBN), which are common azo initiators at present. Thermal hazards are closely related to the reaction kinetics of the substance itself. The form of the reaction, the apparent activation energy and the thermodynamic parameters of the exothermic mode were also obtained.

Kinetic analysis of the actual process using the experimental data of the isothermal calorimetry model is rarely used in the evaluation of related thermal hazard characteristics. The simulation results revealed the kinetic azo models and were further applied to calculate the runaway situations of azo under specific boundary conditions.

70. *Tsai, Chia-Feng, Wen, I-Jyh, Evaluation of Thermal Hazard Properties of Low Temperature Active Azo Compound under Process Conditions for Polymer Resin in Construction Industries Processes (2021), V. 9(11), https://doi.org/10.3390/pr9111934*

Abstract.

The application of polymerization initiators in a process can improve reaction efficiency and reduce energy loss. Azo compounds (azos) provide the required energy and promote polymerization for construction due to the heat release in the decomposition reaction. However, the heat release also brings related thermal hazards due to the lack of proper control. To reduce and avoid possible future hazards, the new azo initiators, 2,2′-Azobis(2-methylpropionamide)dihydrochloride (AIBA) is selected to explore the related thermal properties that are less studied by past literature. For the chemical process, its chemical reaction mechanism is extremely essential. In addition to being an influential foundation for process control, it is also used as a calculation basis for subsequent thermal hazard parameters, which is suitable for evaluating the degree of thermal hazard and emergency response. The assessment program includes kinetic model simulations and consecutive calculation on thermal safety parameters, such as TMRad and TCL for process operations. This study combines the thermogravimetric data with the nonlinear kinetics fitting on thermogram. The fitting results are derived back to the analysis formula which corresponds to the reaction mode to obtain the elementary reaction parameters and establish the kinetics process. The runaway mode and consequent thermal hazard parameters can also be obtained.

Keywords: polymerization, construction, thermal hazard, thermal safety, kinetic

71. *Cao, CR., Chen, WC., Jhang, WC. et al. Thermal decomposition and evaluation thermokinetic parameters for explosive type. J Therm Anal Calorim 144, 443–454 (2021). https://doi.org/10.1007/s10973-020-10475-7*

Abstract.

In Taiwan, due to intensive religious ceremonial activities, the flying and pyrotechnic fireworks of firecrackers are commonly used. In the course of the activities, the use of water as a cooling measure has been pointed out in the past literature that it may cause pyrotechnic materials to deteriorate and reduce their thermal stability. To determine the possible influence of water addition on pyrotechnic deterioration, this study estimates the degree of thermal hazard of pyrotechnic based on the analysis of heat release, reaction kinetics, and the heat exchange model of pyrotechnic deterioration. The explosion sound (ES) firecracker was used to analyze the thermal hazard and mixed water (ES + W) to simulate the dampness condition using differential scanning calorimetry. Thermodynamic equations simulating thermal hazard safety parameters, combined with thermokinetic and thermal runaway data results, were used to discuss the safety and potential thermal hazard characteristics of ES, as the safety of fireworks in storage, transportation, process conditions, and operation assessment to curtail the probability of accidents. The results showed that if the initial exothermic temperature of ES + W is higher than ES, a thermal decomposition reaction will occur at a lower temperature, and the exothermic heat rises and the apparent activation energy decreases, indicating that the ES will increase its instability after being damp. The presence of water degenerated the ES and resulted in a violent reaction during the release process to explode the ES, which increased the chance of accidents among the onlookers.

72. *Liu, SH., Wang, YR., Cao, CR. et al. Systematic process hazard assessment of three kinds of solid organic peroxides with kinetic analysis and heat transfer equilibrium. J Therm Anal Calorim 145, 451–466 (2021). https://doi.org/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.

73. *Ma, XH., Tan, JS., Wei, ZY. et al. Thermal safety study of (5,6-(dicarboxylate)-pyridin-3-yl) methyl-trimethyl ammonium bromide based on decomposition kinetics. J Therm Anal Calorim 145, 2431–2439 (2021). https://doi.org/10.1007/s10973-020-09755-z*

Abstract.

The thermal hazard of (5,6-(dicarboxylate)-pyridin-3-yl) methyl-trimethyl ammonium bromide (DPTAB) was evaluated by carrying out dynamic tests on a differential scanning calorimeter, and the thermodynamic parameters were obtained. A kinetic model was established by simulating experimental curves. The model contains two successive self-accelerating stages, and this article aims to explain the effect that these two stages have on the decomposition of DPTAB, respectively. The thermal behaviors were simulated under isothermal, adiabatic, heat-transfer limited conditions, and the results suggest that the decomposition of DPTAB is uncontrollable as it occurs, and the heat dispersed is intense. The self-accelerating decomposition temperature of DPTAB was 110.9 °C, indicating that the storage and transformation temperatures of DPTAB should not be higher than 110.9 °C. The thermal runaway system reached the maximum reaction rate at a temperature of 139.9 °C within 24 h under adiabatic conditions, thus implying that the processing temperature in industrial applications should be maintained below 139.9 °C.

74. *X-Q. Zhao, W-Q. Wu, H-B. Li, Z-C. Guo, W-H. Chen, L-P. Chen, Thermal hazards of benzaldehyde oxime: Based on decomposition products and kinetics analysis by Adiabatic calorimeter. Process Safety and Environmental Protection, (2021), https://doi.org/10.1016/j.psep.2021.06.030.*

Abstract.

As a self-reactive substance, benzaldehyde oxime (BO) is prone to a highly exothermic runaway reaction and thermal hazard analysis and the reaction kinetics calculation of BO have great significance. In this work, the decomposition products of BO in nitrogen atmosphere were identified by GC-MS and HPLC techniques. The impact of the decomposition products on the decomposition behaviors of BO were analyzed by comparison of the ARC test results of pure BO and mixture of BO and decomposition products. It was found that N-benzylidene benzylamine was the intermediate decomposition product and benzoic acid, benzamide, N-benzyl benzamide, and 2,4,5-triphenylimidazole were the final products of BO. A two-step continuous autocatalytic reaction model was established to depict the decomposition process of BO. The kinetic parameters of the model were calculated by applying the nonlinear optimization method. Finally, thermal behaviors under different process temperature were predicted based on the kinetic model, and the time to maximum rate (TMRad) was predicted as 112.04 °C under 24 h, and 122.19 °C of 8 h, which offer crucial safety information to optimize the safety conditions of BO during usage, storage and transportation, which minimizes the industrial disasters.

Keywords: Benzaldehyde oxime; Thermal hazards; ARC; Product analysis; Kinetics-based simulation

75. **Bao, F., Li, Y., Li, J. et al. Thermal decomposition kinetics and thermal hazards simulation of sodium and rubidium 3,3'-dinitrimino-5,5'-bis(1H-1,2,4-triazole). J Therm Anal Calorim 146, 717–724 (2021). https://doi.org/10.1007/s10973-020-10042-0**

Abstract

Sodium 3,3′-dinitrimino-5,5′-bis(1H-1,2,4-triazole) (Na2DNABT) and rubidium 3,3′-dinitrimino-5,5′-bis(1H-1,2,4-triazole) (Rb2DNABT) were synthesized and characterized by IR spectroscopy and 1H/13C NMR. Rb2DNABT was characterized by single-crystal X-ray diffraction. The thermal decomposition kinetics and thermal hazards of Na2DNABT and Rb2DNABT were investigated by difference scanning calorimeter (DSC) and accelerating rate calorimeter (ARC). The thermal decomposition kinetics (activation energy, pre-exponent, reaction model) were evaluated by Thermal Safety Software (TSS) on DSC and ARC tests. The activation energy of Na2DNABT and Rb2DNABT by DSC test was also calculated by Starink method, which consistent with the simulated activation energy by TSS. Time to maximum rate (TMR), reaction temperature at which TMR is 24 h (TD24) and time conversion limit (TCL) were simulated by TSS, too. The TD24 of Na2DNABT and Rb2DNABT were calculated as 215.86 and 141.95 °C, respectively, and their TCL at 200 °C was calculated as 24.00 and 4.56 h, respectively. Na2DNABT is a stable and safety compound compared with Rb2DNABT.

Keywords: Na2DNABT, Rb2DNABT, Thermal decomposition kinetics, Thermal hazards, TSS

76. **Tsai, Chia-Feng, Wen, I-Jyh, Evaluation of Thermal Hazard Properties of Low Temperature Active Azo Compound under Process Conditions for Polymer Resin in Construction Industries - Processes, (2021) V. 9, Issue 11, 11 p. https://doi.org/10.3390/pr9111934**

Abstract

The application of polymerization initiators in a process can improve reaction efficiency and reduce energy loss. Azo compounds (azos) provide the required energy and promote polymerization for construction due to the heat release in the decomposition reaction. However, the heat release also brings related thermal hazards due to the lack of proper control. To reduce and avoid possible future hazards, the new azo initiators, 2,2′-Azobis(2-methylpropionamide)dihydrochloride (AIBA) is selected to explore the related thermal properties that are less studied by past literature. For the chemical process, its chemical reaction mechanism is extremely essential. In addition to being an influential foundation for process control, it is also used as a calculation basis for subsequent thermal hazard parameters, which is suitable for evaluating the degree of thermal hazard and emergency response. The assessment program includes kinetic model simulations and consecutive calculation on thermal safety parameters, such as TMRad and TCL for process operations. This study combines the thermogravimetric data with the nonlinear kinetics fitting on thermogram. The fitting results are derived back to the analysis formula which corresponds to the reaction mode to obtain the elementary reaction parameters and establish the kinetics process. The runaway mode and consequent thermal hazard parameters can also be obtained.

Keywords: polymerization, construction, thermal hazard, thermal safety, kinetic

77. **S. Weng, W. Wu, Z. Guo, F. Meng, Y. Chen, W-H. Chen, The Formation Mechanism and Thermal Decomposition Kinetics of 2,4,6-Trinitroresorcinol in the Dinitrobenzene Production, Process Safety and Environmental Protection, 2021, Journal pre-print https://doi.org/10.1016/j.psep.2021.11.014.**

Abstract

2,4,6-Trinitroresorcinol (TNR), one main by-product in the dinitrobenzene (DNB) production process, is self-reactive substance and has led to tragic explosion incidents in China. In this article, the formation mechanism of TNR during the DNB production process was studied employing HPLC and HPLC-MS technique. Thermal decomposition behavior of TNR was also systematically studied by differential scanning calorimeter (DSC). The decomposition kinetics of TNR were investigated employing both iso-conversional (Friedman and Ozawa method) and model-fitting method. The formation mechanism of TNR during the dinitrobenzene (DNB) production is confirmed: The two by-products of dinitrophenol (DNP) and trinitrophenol (TNP) produced in the benzene mononitration stage are further nitrated to form tetranitrophenol (TTNP) in the mononitrobenzene (MNB) nitration stage. Then most of TTNP will be hydrolyzed to form the TNR during the water washing process. The decomposition process of TNR has been proven to follow three consecutive steps (A→B1→B2→B). The former two steps present autocatalytic behavior while the last step obeys N-order reaction model. The accuracy of the developed decomposition model and the obtained model parameters have been demonstrated by the comparison of the simulated and experimental DSC data and the activation energy obtained by both the iso-conversional method and model-fitting method. The same trend of experimental and simulated results about isothermal reaction further verify the building model.

Keywords: 2,4,6-Trinitroresorcinol; Nitration; Thermal decomposition; Autocatalysis; Formation mechanism; Tetranitrophenol

78. **Zhen-Yun Wei, Ji-Shuang Tan, Xiao-Hua Ma, Rong Kong, Xuan Liu, Chun-Sheng Cheng, and San-Xi Li, Research on Thermal Decomposition Kinetics and Thermal Safety for a New Epoxiconazole Crystal, ACS Omega 2021 6 (8), 5582-5590, DOI: 10.1021/acsomega.0c05988**

Abstract

To clarify the thermal safety inherent in a new epoxiconazole crystal, diﬀerential scanning calorimetry (DSC) and adiabatic accelerating rate calorimetry (ARC) were used for testing and research. The Friedman method and model method were used to analyze thermal decomposition kinetics based on the DSC data, and the N-order and autocatalytic decomposition reaction kinetic models were established. The double scan method was utilized to verify the autocatalytic eﬀect during the decomposition process. The Friedman method, N-order, and autocatalytic model methods were used to study the substance's thermal decomposition characteristics. ARC data are utilized to verify the aforementioned prediction results and the kinetic parameters that were obtained

based on ARC data from N-order and autocatalytic model methods that concur with the simulation results. This paper applies the N-order and autocatalytic model to the kinetic model to further predict thermal safety parameter time to maximum rate under adiabatic conditions.

79. *Tsai, C.-F.; Wen, I.-J. Evaluation of Thermal Hazard Properties of Low Temperature Active Azo Compound under Process Conditions for Polymer Resin in Construction Industries. Processes 2021, 9, 1934. https://doi.org/10.3390/pr9111934*

Abstract

The application of polymerization initiators in a process can improve reaction efficiency and reduce energy loss. Azo compounds (azos) provide the required energy and promote polymerization for construction due to the heat release in the decomposition reaction. However, the heat release also brings related thermal hazards due to the lack of proper control. To reduce and avoid possible future hazards, the new azo initiators, 2,2′-Azobis(2-methylpropionamide)dihydrochloride (AIBA) is selected to explore the related thermal properties that are less studied by past literature. For the chemical process, its chemical reaction mechanism is extremely essential. In addition to being an influential foundation for process control, it is also used as a calculation basis for subsequent thermal hazard parameters, which is suitable for evaluating the degree of thermal hazard and emergency response. The assessment program includes kinetic model simulations and consecutive calculation on thermal safety parameters, such as TMRad and TCL for process operations. This study combines the thermogravimetric data with the nonlinear kinetics fitting on thermogram. The fitting results are derived back to the analysis formula which corresponds to the reaction mode to obtain the elementary reaction parameters and establish the kinetics process. The runaway mode and consequent thermal hazard parameters can also be obtained.

Keywords: polymerization; construction; thermal hazard; thermal safety; kinetic

80. *Chia-Feng Tsai, I-Jyh Wen, Shang-Hao Liu, Chen-Rui Cao, Han Zhang, Evaluation of thermal hazard characteristics of four low temperature reactive azo compounds under isothermal conditions, Journal of Loss Prevention in the Process Industries, V. 71, 2021, 104453, ISSN 0950-4230, https://doi.org/10.1016/j.jlp.2021.104453.*

Abstract

The polymerization reaction can lower the threshold of the required energy by the initiator to improve the efficiency of the overall process reaction. Emerging polymerization initiators are also a major focus of process improvement and technological progress. Azo compounds (azos), which used in dyeing applications, are subsequently used in polymerization reactions due to their highly exothermic reaction characteristics.

Although higher heat release can promote polymerization and modify the product, heat generation may also cause process hazards. These thermal hazard parameters were studied by selecting dimethyl 2,2′-azobis(2,4-dimethylvaleronitrile) (ABVN), 2,2′-azobis(2-methyl propionate) (AIBME), 2,2′-azobis(2-methylpropionamide) dihydrochloride (AIBA), and 2,2′-azobis(isobutyronitrile) (AIBN), which are common azo initiators at present.

Thermal hazards are closely related to the reaction kinetics of the substance itself. The form of the reaction, the apparent activation energy and the thermodynamic parameters of the exothermic mode were also obtained. Kinetic analysis of the actual process using the experimental data of the isothermal calorimetry model is rarely used in the evaluation of related thermal hazard characteristics. The simulation results revealed the kinetic azo models and were further applied to calculate the runaway situations of azo under specific boundary conditions.

Keywords: Initiator; Process improvement; Reaction characteristics; Reaction kinetics; Thermal hazard

81. *Zhang, J., Ma, Y., Dong, Z., Wang, SY. et al. Numerical simulation to study and optimize the significant hidden temperature gradients in adiabatic tests. J Therm Anal Calorim 146, 919–935 (2021). https://doi.org/10.1007/s10973-020-09972-6*

Abstract

In adiabatic thermal analysis, correct measurement of temperature is usually ensured by means of a calibration procedure and thermal inertia corrections. However, there is a significant gradient within system, which not only makes the obtained test results inaccurate, but also causes serious errors in subsequent kinetic calculations and thermal risk assessment. Thus, estimations of the temperature gradients, which appear into the sample, are of highest interest to choose the right operational conditions that minimize that gradient. In this work, the CFD software has been applied to study this temperature gradient issue in adiabatic system. In view of the causes of temperature gradients, the influencing factors and the resulting analysis errors are all deeply researched. In addition, three different kinds of adiabaticity control model cases have also been simulated to explore the right operational conditions that minimize gradient and provide more reliable kinetics and thermal hazard parameters (Q∞, k0, Ea, n, TD24, TCL). After a comparative study, the authors define the more reliable operational conditions, which include selecting a suitable temperature response value and the adiabatic temperature control model. Finally, the reliability of the adiabaticity control model that achieves the minimum temperature gradients and provides the most accurate calculation results was verified through the different adiabatic tests.

82. *Chia Xu Peng, Shunyao Wang, Weiguo Cao, Chi-Min Shu, Assessing reactive hazard by coupling computational fluid dynamics with a descriptive kinetic model to resolve the scale-up problem, Journal of the Taiwan Institute of Chemical Engineers, 133 (2022), ISSN 1876-1070, https://doi.org/10.1016/j.jtice.2022.104264*

Abstract

Background: The scale-up problem has long been considered a major challenge in reactive hazard assessment, because laboratory scale experimental results cannot be directly applied to the real industry.

Method: To resolve this problem, a new method of coupling computational fluid dynamics (CFD) with the descriptive kinetic model was proposed herein, which determined the thermal decomposition reaction progress of cumene hydroperoxide (CHP) in different scale reactors. The descriptive kinetic model was evaluated through differential scanning calorimetry (DSC) experiments.

Significant findings: The new method was verified by comparing the simulation and experimental results in a medium-scale pressure vessel. The thermal explosion induction period of CHP in an industrial-scale storage tank under fire conditions was predicted. The complex phenomena and mechanisms of CHP thermal decomposition in the storage tank were also elucidated and discussed. This study explored the dynamic decomposition process of CHP, and the results can be applied for increasing the accuracy of reactive hazard assessment

83. *Wen-qian Wu, Ze-yuan Xia, Wang-hua Chen, Li-ping Chen, Hua-bo Li, Zi-chao Guo, Effect of melting on the thermal hazard of anthraquinone dyes waste, Organic Process Research & Development (2022), DOI: 10.1021/acs.oprd.1c00493*

Abstract

The thermal decomposition of the typical hazardous anthraquinone dyes wastes was tested through the differential scanning calorimetry, and the components interaction was analyzed through model-free method. The test results show that melting makes the solid-phase decomposition of 1,5-dinitroanthraquinone decreased as that the activation energy is reduced by about 142.08kJ/mol. And the activation energy of the third step decomposition of the mixture is reduced. The spatial configuration of each substance was descripted based on quantum mechanics tools. The calculation results of the laplace bond show that the middle ring bond is broken with the left of nitro group, and the polynitro substance needs to remove the -CO group to form a stable phenylacetylene group which can react with anthraquinone. The reactivity rating number classification was simulated by the kinetic equation obtained by the model fitting method in the extreme fire conditions. It shows that mixture without anthraquinone has the characteristics of higher heat production rate and overall heat effects under high temperature. The melting effect of anthraquinone will make the mixture more stable except under elevated temperature and pressure.

84. *Chia-Feng Tsai and I-Jyh Wen, Assessment of the Thermal Hazard Characteristics of Three Low-Temperature Active Azo Initiators for Polymer Resin in Construction Industries under Adiabatic Conditions, ACS Omega (2022). doi.org/10.1021/acsomega.1c06269,*

Abstract

Resins continue to occupy a place in the waterproof building market. Unlike traditional concrete building materials, the polymerization of resins requires initiators to support the required energy to drive the reaction or reduce the polymerization threshold, which shows a high reaction rate and low energy consumption in the polymerization process. Azo compounds (azos) are energetic substances commonly used in polymerization, but they can cause process hazards due to the amount of heat release and accumulation of the resulting heat. To ensure that similar hazards do not occur, the emerging azo initiators 2,2′-azobis(2-methylpropionamide)dihydrochloride (AIBA), 2-cya- nopropan-2-yliminourea (CABN), and 2,2′-azodi(2-methylbutyronitrile) (AMBN) are explored. Depending on the process conditions, it is critical to examine how chemical reactions from a laboratory behave at a large scale. Kinetic models can be used to estimate fundamental safety parameters suitable for assessing the reaction hazards and as control measures, such as time to the maximum reaction rate under adiabatic conditions, time to the conversion limit, and runaway determination for process operation. The structure of this study is a combination of adiabatic calorimeter data and a nonlinear adiabatic dynamics model with the goal of helping to fill the void in research on thermal hazard analysis of emerging azo initiators. The adiabatic data is used to analyze the reaction mode characteristics of the azo compounds, and combined with the external environment, the reaction and temperature parameter changes of the azo compounds due to the reaction are discussed in the actual situation.

85. *Gosteva, A., Kossoy, A., Tsvetov, N. et al. Dynamics of Thermal Decomposition of the Double Complex Salt [Cr(ur)6][Co(CN)6]?4Í2Î. Russ. J. Inorg. Chem. (2022). https://doi.org/10.1134/S0036023622080150*

Abstract

Information on the thermal decomposition of the double complex salt (DCS) $[Cr(ur)_6][Co(CN)_6]\cdot 4H_2O$ (ur is urea $CO(NH_2)_2$) in the temperature range of 30–1000°C has been presented. The thermolysis of the studied DCS has been carried out in an argon atmosphere at three heating rates (5, 10, 20°C/min). The obtained TG data have been processed using the ARKS TA, and then the kinetics has been evaluated by the ARKS FK program from data for 5 and 10°C/min. The proposed multi-stage formal kinetic model provided a good fit of experimental data and showed a very reasonable prediction of decomposition at a rate of 20°C/min. It was demonstrated the formation of cyanobridge structures during thermolysis. A metastable compound Co_3Cr was found in the product of thermolysis at 550°C. The mixture of the final products of calcination has been comprised Co^0 (α-face-centered cubic lattice (fcc), β-fcc), Cr_2O_3, Cr_7C_3, $Cr_{23}C_6$, $Cr_{21.26}Co_{1.74}C_6$.

86. *Chen Yao, Ye-Cheng Liu, Chi-Min Shu et ll, Thermal Stability Determination of Propylene Glycol Sodium Alginate and Ammonium Sulfate with Calorimetry Technology, Processes 2022, 10, 1177.* <u>*https://doi.org/10.3390/pr10061177*</u>

Abstract

Propylene Glycol Alginate Sodium Sulfate (PSS) is widely produced and used in medicine as a marine drug for treating hyperlipidemia. During the sulfonation synthesis of PSS, the sulfonation of chlorosulfonic acid is exothermic. At high temperatures, the process can easily produce a large amount of ammonium sulfate. Ammonium sulfate adheres to PSS in crystal and participates in the sulfonation reaction. In this study, the sulfonation process of commercial PSS was reproduced in the laboratory using chlorosulfonic acid and formamide. We used differential scanning calorimetry and thermogravimetric analyzer to examine the thermal

stability of PSS, and we used both differential and integral conversional methods to determine the appropriate thermokinetic models for this substance. We also established an autocatalytic model to study the conversion limit time and the maximum rate time of this substance. After calculation, the activation energy of this substance is no more than 60 kJ/mol, and it has other exothermic performances at different heating rates. The results help to optimize the sulfonation process of PSS and analyze the thermal risk of PSS with ammonium sulfate.

Abstract

Bis(1-(tert-butylperoxy)-1-methylethyl)-benzene (BIPB) is susceptible to thermal runaway or explosion when exposed to metal ions or acid during production. In this article, thermal decomposition of BIPB and its thermal sensitivity to metal ions and acid were firstly systematically studied by DSC and ARC. Experiments demonstrate that BIPB decomposes around 105-115°C with ΔH^- of 1483.78J·g−1. $FeCl_3$ and H_2SO_4 have a more pronounced impact on the thermal decomposition characteristics of BIPB compared with other impurities. Furthermore, the effect became more pronounced with increasing H_2SO_4. The model-free and model-fitting methods were combined to determine BIPB's decomposition as a two-step consecutive n-order reaction (A→r1B→r2C), then to evaluate thermal hazard indicators. Ultimately, two sem-quantitative risk assessment methods were separately used to evaluate thermal risk of compounds and processes. It's shown that the MF of BIPB mixtures doped with $FeCl_3$ is highest, 2, and the Borda index of the purification process in BIPB synthesis is 44 and risk rank is 2, which is an unacceptable risk.

Keywords: Bis(1-(tert-butylperoxy)-1-methylethyl)-benzene; Numerical simulation; Reaction kinetics; Impurity thermal effect; Thermal hazards assessment

Abstract

Bis(1-(tert-butylperoxy)-1-methylethyl)-benzene (BIPB) is susceptible to thermal runaway or explosion when exposed to metal ions or acid during production. In this article, thermal decomposition of BIPB and its thermal sensitivity to metal ions and acid were firstly systematically studied by DSC and ARC. Experiments demonstrate that BIPB decomposes around 105-115°C with ΔH^- of 1483.78J·g−1. $FeCl_3$ and H_2SO_4 have a more pronounced impact on the thermal decomposition characteristics of BIPB compared with other impurities. Furthermore, the effect became more pronounced with increasing H_2SO_4. The model-free and model-fitting methods were combined to determine BIPB's decomposition as a two-step consecutive n-order reaction (A→r1B→r2C), then to evaluate thermal hazard indicators. Ultimately, two sem-quantitative risk assessment methods were separately used to evaluate thermal risk of compounds and processes. It's shown that the MF of BIPB mixtures doped with $FeCl_3$ is highest, 2, and the Borda index of the purification process in BIPB synthesis is 44 and risk rank is 2, which is an unacceptable risk.

Keywords Bis(tert-butylperoxy isopropyl) benzene peroxide (BIBP)· Thermal runaway· Autocatalysis reactions· Thermal damage· Thermal hazard

Abstract

Accelerating Rate Calorimetry (ARC) is a widely used adiabatic calorimetry technique to evaluate thermo- kinetics of hazardous chemical reactions. Most ARCs rely on measurement of temperature at the external wall of the ARC sphere to evaluate the temperature rise rate, and therefore exothermic reaction rate. We report large temperature gradients between the center and wall for a granulated solid sample tested using an un-stirred ARC that leads to varying spatiotemporal temperature profiles. Such gradients were found to be significantly lowered in organic liquid samples, enabling classifying some granulated solid samples as heat transfer-limited systems. This study reveals that such temperature gradients obviate estimation of representative exothermic reaction rate, manifesting in hazard underestimation through erroneous pressure and apparent conversion profiles. Next, the addition of an inert was demonstrated to reduce the magnitude of such gradients, thereby enabling relatively accurate hazard assessment and offering a potential solution. Lastly, several strategies are outlined to allow researchers to identify and mitigate the influence of gradients during hazard assessment. Researchers must be cognizant of the potential for gradients when analyzing and interpreting ARC data for thermo-kinetic modeling and hazard evaluation. During hazard evaluation, researchers should confirm that no significant gradients exist or find ways to de-sensitize their hazard assessment parameters if gradients exist and cannot be minimized..

Keywords Accelerating Rate Calorimetryб Exothermic, Thermal lag, Adiabatic Calorimetry, kinetics, Hazard assessment

CISP comment. Note that CISP software had not been used in this work though the authors are among software users. Nevertheless the article has been included in this list because the authors share and brilliantly develop some ideas proposed by the CISP experts.