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Thermal behaviour of acrylonitrile polymerization and polyacrylonitrile decomposition

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Abstract

The microcalorimetric studies on the polymerization of acrylonitrile with and without the thermal influence of polyacrylonitrile decomposition provide vital information on its thermal sensitivity and intrinsic safety. The present studies indicate that the exothermicity of polymerization and decomposition of polyacrylonitrile are kept under check by the self-regulatory role of the aqueous medium. However, the polymer drying operation is more prone to thermal hazards under unregulated temperature regime. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chain polymerization reactions are exothermic in nature and some of the polymeric products are classified as thermally sensitive. Polyacrylonitrile (PAN), an industrially important polymer for carbon fiber manufacture, falls in this category [1,2]. It is commercially produced batch-wise through aqueous polymerization at about 50–60°C with an appropriate initiator (e.g. potassium persulfate). The suspended polymer in the

Abbreviations: A , Arrhenius frequency factor (s^{-1}); C_0 , Initial reactant concentration; E , Activation energy (kcal mole^{-1}); n , Reaction order; k^* , Pseudo zero order rate constant (s^{-1}); R , Universal gas constant ($\text{J mole}^{-1} \text{R}^{-1}$); t , Time (s); T , Temperature at any time ($^{\circ}\text{C}$); T_f , Final temperature ($^{\circ}\text{C}$); ΔT_{ad} , Adiabatic temperature rise ($^{\circ}\text{C}$); dT/dt , Self-heat rate ($^{\circ}\text{C s}^{-1}$); M_m , Self-heat rate at T_m ($^{\circ}\text{C s}^{-1}$); M , Self-heat rate at T ($^{\circ}\text{C s}^{-1}$)

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reactor can be as much as 50% by weight of the reactor contents. The polymer is subsequently dried under a nitrogen atmosphere. Under normal operating conditions, the low solubility [3] of acrylonitrile (AN) in water (about 1.2 mole l^{-1} at 25°C) and the presence of large quantity of aqueous medium can provide the self-regulatory mechanism that is needed for the control of exothermicity. The drying of PAN, on the other hand, encounters totally different conditions for thermal energy regulation. The objective of the present study is to examine the thermal responses of these two operations through microcalorimetric studies.

Deviations from normal operating conditions do occur in process plants owing to failure of control instruments and equipments and unforeseen human errors [4,5]. Therefore, it is of interest to assess the intrinsic safety of PAN production and post-processing operations under the influence of unanticipated process deviations. It is well-known that thermal excursions beyond the normal operating limits may contribute to thermal runaway situations in polymerization reactors due to exothermicity generated on account of speed-up of the rate of main reaction and in situ decomposition of the reactants or products [6]. Highly sensitive microcalorimetric techniques are currently available to precisely quantify the exothermic activity [9] of such reactions. Adiabatic temperature and pressure rise, onset and maximum temperature limits to thermal runaway and composition of volatile and gaseous products have become measurable parameters for assessing the intrinsic safety of thermally sensitive reactions.

2. Experimental

2.1. Accelerated rate calorimetry (ARC)

Thermal investigations have been carried out employing ARC of the Columbia Scientific Instruments (USA) for studying the thermal runaway behaviour of AN polymerization augmented by the thermal decomposition of PAN. The theoretical and operational aspects of ARC has been well-documented in the literature [7,8]. In a typical ARC run, the sample reaction mixture is placed in the bomb and its temperature increased incrementally (by 5°C in each step) from a pre-determined initial temperature and held at each step for a specific time period to look for unaided exothermic activity. In its absence, the heat-wait-search procedure is continued until a measurable rate of exothermic activity ($> 0.02^\circ\text{C min}^{-1}$) is detected or pre-determined final temperature is attained without any positive thermal input. The extent of condensable and non-condensable gaseous product evolution is obtained from the pressure recordings made before and after cooling the bomb to the ambient conditions.

2.2. Reaction calorimetry (RC)

The Reaction Calorimeter (Mettler RC1) is a computer-controlled stirred reactor which can be operated in a batch or a semi-batch mode under isothermal or adiabatic conditions. It is equipped with adequate instrumentation to measure the heat of the reaction, specific heat of the reaction mixture, cooling load requirement, overall heat

transfer coefficient and other thermal parameters. The AN polymerization is conducted in RC, under simulated commercial reactor conditions. The post-reaction operations include filtration and drying of the polymer.

2.3. Pyrolysis gas chromatography

A curie point pyrolyser (JHP 3) of Japan Analytical Industry Co., which is coupled directly to GC-MS (Shimadzu QP 2000) and the chromatographic separation is employed for the studies. It is equipped with a DB 1 > 01 column employing helium as a carrier gas. The heating rate is programmed at $10^{\circ}\text{C min}^{-1}$ for 40°C to the desired temperature and the isothermal conditions are maintained. The PAN sample is wrapped in a ferromagnetic pyrofoil and exposed to pyrolysis temperatures from 200 to 590°C .

3. Thermal analysis

High Pressure Differential Scanning Calorimeter (HPDSC), Differential Thermal Analyser (DTA) and Thermo Gravimetric Analyser (TGA) are employed for the thermal analysis of PAN decomposition for a sample size of 5–10 mg, employing heating rates in the range of $5\text{--}20^{\circ}\text{C per min}$.

4. Theoretical

The self-heat rate, as measured by ARC, is of practical value to understand the thermokinetics of AN polymerization and PAN decomposition. Assuming that the mass of the reaction mixture and its heat capacity are constant, a thermal balance of the system provides the following relationship between the self-heat rate to a kinetic event [9].

$$\frac{dT}{dt} = k \left[\frac{T_f - T}{\Delta T_{ad}} \right]^n C_O^{n-1} \Delta T_{ad} \quad (1)$$

$$k * = KC_O^{n-1} = \left[\frac{dT/dt}{\Delta T_{ad}} \right] \left[\frac{\Delta T_{ad}}{T_f - T} \right]^n = Ae^{-E/RT} C_O^{n-1} \quad (2)$$

A plot of $\ln k *$ vs. $1/T$ is expected to be a straight line, provided the order of the reaction is correctly chosen. The reaction velocity constant, $k *$ can be determined at any temperature from Eq. (2). On relaxing the conditions of mass and heat capacity consistency, Eq. (2) can be simplified [10]. The activation energy of the thermal event can be estimated from the time to maximum rate (TMR) which is defined as:

$$T_m = RT^2 M / M_m E$$

Usually, the critical parameters of interest for the design of a reactor are (i) cooling load for quenching the reaction mass and (ii) the time to maximum rate (TMR), i.e., the actual time available for remedial action. The reactor quenching is practicable only at the initial stage of the reaction runaway. The magnitude of the TMR is dictated by the peak value of the self-heat rate.

5. Consequences of unwanted events in AN polymerization

The following are the major events that may contribute to an emergency situation in AN polymerization.

- cooling and heating system failures
- agitator failure
- malfunction of chemical charge system

5.1. Cooling and heating system failures

They could occur due to maloperation or failure of valves, pumps and controls associated with the reactor cooling water system or overhead vent unit. In less frequent cases, piping of the condensers could become plugged or heat exchanger (in the cooling circuit) surface could become excessively fouled due to bad maintenance. These may contribute to total or partial cooling system failure. The heating system (steam) employed for initial heating of the charge and for maintaining the temperature (optional) during the last phases of the reaction, can also fail due to similar reasons. Cooling/heating systems, when they are stretched beyond their design limits, normally contribute to pressure/temperature hikes in spite of the intrinsic heat-sink capacity of the reaction medium.

5.2. Agitator failures

They can occur due to electrical or mechanical problems. The heat removal capability of a reaction system greatly depends on the overall heat transfer coefficient which is a function of the degree of mixing of the reactor contents, heat transfer capabilities of coolant and vessel wall. Thus, the stoppage of agitator generally leads to loss of control rhythm and occurrence of hot spots in the reaction mass in bulk or solution polymerizations. However, in AN polymerization, the slurry phase will create less heat accumulation problems and can be neglected for emergency situation analysis.

5.3. Defective charge system

Failure of feed charging system due to instrumental malfunctioning or human errors could result in dosing of excess initiator or monomer or an upset in monomer to initiator proportion. This could lead to unwanted side reactions. It may be noted that AN is soluble only to an extent of 7% in water and beyond this limit, it remains as separate layer in unstirred condition. It does not participate in most part of the polymerization

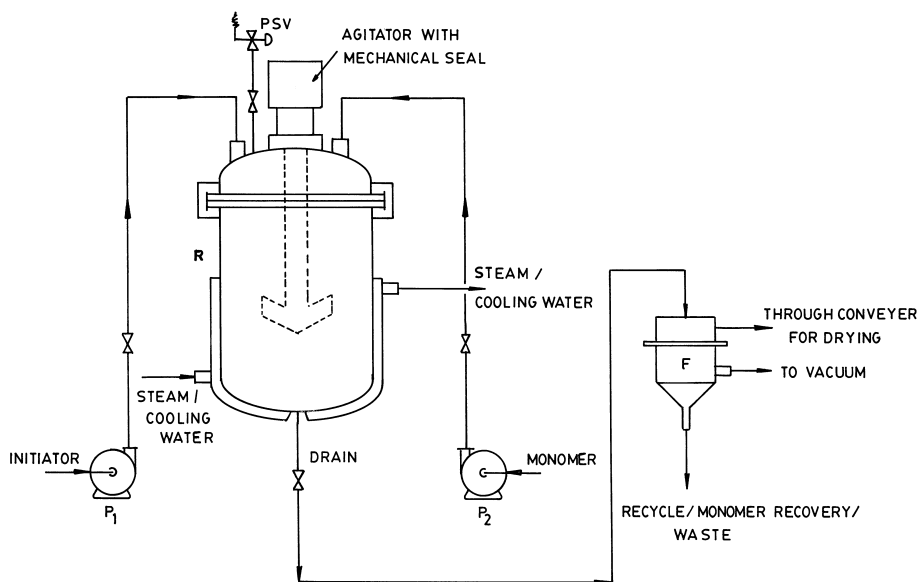


Fig. 1. Typical process system for AN polymerization.

process as the initiator is insoluble in AN. In view of this, consequence of charge system failure in AN polymerization will be very marginal.

6. The commercial reaction system

PAN is commercially produced in agitated batch reactors (Fig. 1) employing aqueous medium at a temperature not exceeding 50–60°C and atmospheric pressure. Potassium persulfate (1.8×10^{-2} mole l^{-1}) is employed as the initiator. The polymerization is conducted in nitrogen atmosphere for a period of 1–2 h depending upon the charge quantity, desired product molecular weight and operating temperature. The polymerization initially takes place in aqueous phase and as the reaction progresses, it gradually shifts to the polymer phase. The reactor is equipped with robust heating and cooling systems to take care of thermal needs of all phases of the reaction. The following data has been considered in this work for the thermal analysis of a typical commercial AN Polymerization Reactor.

Batch size	5000 kg
Reaction temperature	60°C
Coolant temperature	45–50°C
Monomer concentration	1.20 mole l^{-1} (350 kg)
Initiator concentration	1.80×10^{-2} mole l^{-1} (24.598 kg)
Heat transfer coefficient	131.7 W m^{-2} K^{-1}
Heat transfer area	9.06 m^2

7. Operational sequences

The commercial reactor volume is about 8 m^3 for a batch size of 5000 kg. Initially, a mixture of AN (1.20 mole l^{-1} , i.e. $\sim 7\%$) and water (90%) is charged into the reactor. The reactor contents are heated to the desired temperature within the range of 50 to 60°C and the initiator is added prior to the start of other operations. With the progress of polymerization, the reactor contents become heterogeneous as the polymer is insoluble in water, as well as in AN. The reaction being exothermic, an efficient cooling water system is employed. An approach temperature of $10\text{--}15^\circ\text{C}$ between the reaction mass and the coolant temperatures is generally maintained. This is justified, since under normal operating conditions, the presence of a large quantity of aqueous medium ensures quick dissipation of polymerization heat.

8. Results and discussion

The RC studies provided the heat generation (q) pattern in AN polymerization under simulated commercial reactor conditions at 45, 50 and 60°C . A plot of dq/dt vs. temperature (Fig. 2) provides the coolant requirement at these temperatures. ARC data for AN polymerization and decomposition of AN and PN has been presented in Fig. 3 and Table 1. It is clear that the decompositions of AN and PAN set in at 206 and 145°C , respectively, with the corresponding values of ΔT_{ad} at 154 and 259°C and peak heat generation rates of 21.8° and $10^\circ\text{C min}^{-1}$. The pressure profile given in Fig. 4 shows that the decomposition products contribute significantly to the pressure build-up in both cases.

The profile of self-heat generation in the case of the reaction mixture (water + 7% AN + initiator) is shown in Fig. 5 and the experimental results are summarized in

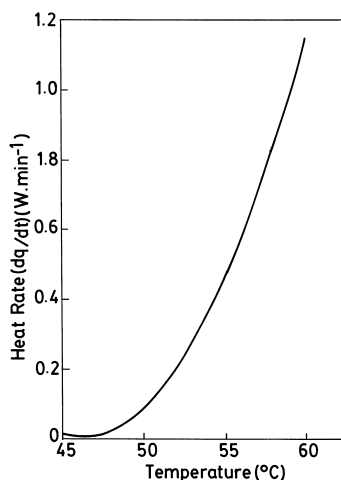


Fig. 2. Heat production rates for AN polymerization reaction.

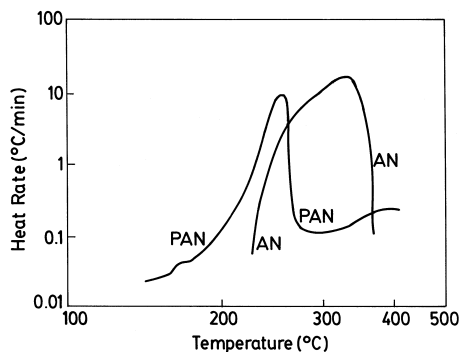


Fig. 3. Self-heat rates of AN and PAN decompositions.

Table 1. Two exothermic peaks in Fig. 3 correspond to the AN polymerization and PAN decomposition, respectively. The heat of polymerization contributes to an adiabatic temperature rise of 28°C with a T_{\max} of 94°C. It is interesting to note that the presence of aqueous medium in polymerization reactor delays the onset of PAN thermal decomposition by nearly 60°C and its adiabatic temperature rise drops very steeply from 260°C to 20°C. The pressure vs. temperature data in Table 1 indicate the pressure contribution of water vapor in the case of AN polymerization and gaseous products in the case of AN and PAN decompositions.

Based on the ARC and RC studies, the thermal stability diagram for AN polymerization has been constructed (Fig. 6). The maximum heat generation rate covering the operational range of 45 to 60°C is plotted as a function of temperature. The heat removal rates corresponding to these temperatures are also plotted on the same diagram. They are represented as straight lines. At 45°C coolant temperature, the stable situation is represented by the heat removal line AB, subject to the condition that the system temperature is lower than T_c , which at point B, is equal to the temperature of no return. Under these conditions, the cooling capacity of the system exceeds the heat generation rate and the temperature of the reactor will drop to the temperature corresponding to point A. Theoretically, the above reaction system can be considered as stable when

Table 1

Arc data for AN polymerization and AN and PAN decomposition

Sample no.	Sample	T onset (°C)	ΔT (°C)	Pressure (psia)		Pressure (psia) on cooling to 25°C
				Total	Vapour	
1.	Acrylonitrile	206.0	153.4	421	–	220
2.	Polyacrylonitrile	145.4	259.6	395	–	79
3. ^a	Reaction mixture (water (90%)+ Acrylonitrile (7%)+ initiator) ^a	204.8	20.0	375	358.8	14.7

^a Isoaging at 60°C followed by heat-wait temperature search.

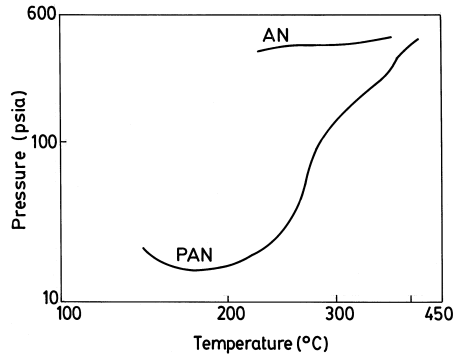


Fig. 4. Pressure profiles of AN and PAN decompositions.

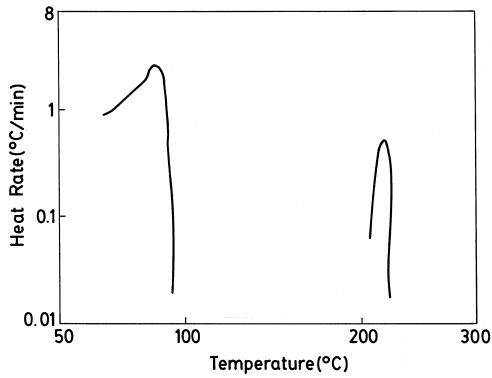


Fig. 5. Self-heat rate for AN polymerization coupled with AN and PAN decomposition.

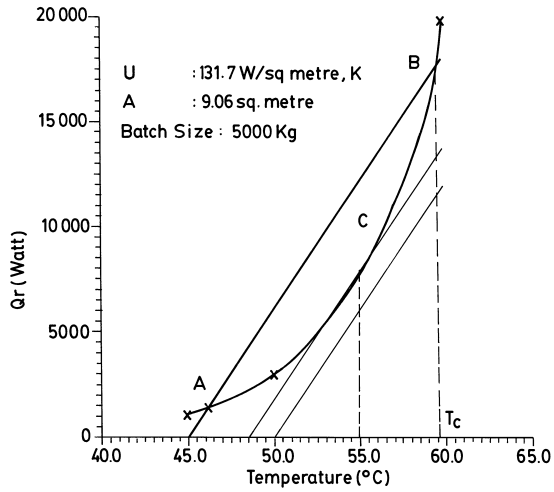


Fig. 6. Heat generation and removal for AN polymerization.

coolant temperature is lower than T_c . However, in practice, the system becomes unstable with only a small deviation in T_c . At a fractionally lower temperature, the system will go to stable point B, but at a fractionally higher temperature, the system will generate more heat than can be removed. Consequently, the temperature of the reaction system tends to increase. At this stage, the dampening role of the aqueous medium on self-heat generation of AN polymerization comes into play to restrict (Fig. 3) the adiabatic temperature rise to 28°C and T_{max} to 94°C . The coolant system failure, therefore, is unlikely to cause any runaway condition in AN polymerization reactor of the 5000 kg batch capacity.

The thermal stability diagram also shows that the system becomes unstable at coolant temperature as represented by point C. It is of practical interest, since it specifies the minimum temperature difference to be maintained between the process and the coolant. At point C, the slopes of the heat removal line and heat generation curves are equal.

The presented analysis has clearly brought out the positive role of the aqueous medium as a thermal moderator in AN polymerization. The observed pressure rise is predominantly due to water vaporization and is amenable to normal pressure relief and cooling system controls. The vent area required for safe release of the generated pressure can be estimated by employing DIERS methodology reported [11] by AIChE. The intrinsic safety of this reactor system is, thus, verifiable.

9. Thermal sensitivity of PAN drying

The thermal decomposition studies on PAN has provided the critical information that is required to assess the vulnerability of PAN dryers to thermal hazards. It is dried commercially in three stages from $109\text{--}125^\circ\text{C}$ as given in Fig. 7. The ARC studies, as reported in the previous section, show that the polymer-drying operation can become vulnerable to thermal hazard of PAN decomposition if the temperature in any of the drying chambers exceeds 140°C . The chamber III of the dryer is relatively more vulnerable, since it has the highest operating temperature (125°C). This temperature difference of 15°C demands a robust control system for the PAN dryer.

The time to reach the maximum rate of PAN decomposition is estimated as 250 min at 160°C . This is the maximum time available for implementing remedial action. It provides reasonable time for operators to bring the situation under control. The peak self-heat rate of PAN decomposition is found to be $10^\circ\text{C min}^{-1}$. The activation energy

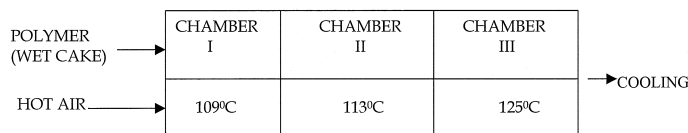


Fig. 7. Multistage drying of polyacrylonitrile.

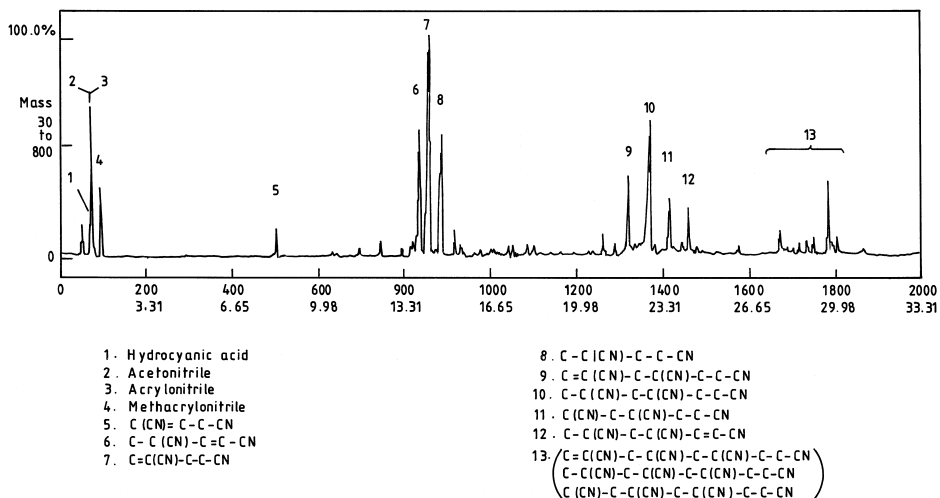


Fig. 8. Pyrolysis gas chromatogram of PAN at 590°C.

of the decomposition process is estimated as 4.52×10^4 kcal mole⁻¹. The heat of decomposition is found to be 213.2 cal per g of PAN.

The thermogravimetric analysis has shown that PAN degradation is exothermic and is accompanied by the liberation of sizeable volume of gaseous products. As per the DTA and DSC thermograms, PAN decomposition is represented by a single exothermic peak. The weight loss due to gas evolution is found to be of the order of 33% w/w. The pyrolysis GC studies on the gaseous products have been carried out at 590°C to identify the nature of evolved gases. The relevant pyrogram is shown in Fig. 8. Approximately 10 signals are observed. For the purpose of this study, the decomposition products are lumped into five categories as given below.

	Percentage w/w
HCN, AN, methacrylonitrile and acetonitrile	13.89
C-C(CN)-C=C-CN	7.84
C-C(CN)-C-C(CN)-C-C(CN)-C-(CN)	4.3
C-C(CN)-C=C(CN)	4.27
C-C(CN)-C-C(CN)-C-C(CN)=C	2.48

Accordingly, for a 5000 kg charge of PAN, the quantum of thermal decomposition products are estimated as the following.

- solid residue: 3350 kg
- volatile products: 1650 kg
- composition of volatile products
 - * low molecular weight components including HCN, AN, acetonitrile, etc.: 229.2 kg
 - * other oligomeric products: 1420.8 kg

Their rate of generation can be computed from the self-heat rate plot (Fig. 3). The PAN drying yard design has to take into account the vent requirement for the safe release of the generated gaseous products.

10. Conclusion

The presented studies, validated with a typical commercial plant data, have unequivocally brought out the moderating role of aqueous medium in the AN polymerization and the verifiability of its intrinsic safety. They also highlighted the vulnerability of PAN dryers to thermal hazard under unregulated temperature regime and inadequate vent arrangements.

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References

- [1] M. Minagawa, M. Okamoto, O. Ishizuka, *J. Polym. Sci., Polym. Chem. Ed.* 16 (1978) 3031.
- [2] M. Minagawa, *J. Polym. Sci., Polym. Chem. Ed.* 18 (1990) 481.
- [3] F.S. Dainton, P.H. Seaman, *J. Polym. Sci.* 39 (1959) 279.
- [4] T. Hoppe, B. Grob, *Proc. Int. Symp. Runaway Reactions, CCPS, MA*, 7–9 March 1989, p. 133.
- [5] R.N. Laudan, *Chem. Eng. Prog.*, April 1993, 66.
- [6] M. Surianarayanan, A. Koshy, K.V. Raghavan, *Proc. IX Natl. Symp. Thermal Analysis, ITAS, Goa, India*, 8–10 November 1993, p. 39.
- [7] M.R. Ottaway, *Analytical Proceedings* 23 (1986) 116.
- [8] Snee, *J. Occup. Acci.* 8 (1987) 261.
- [9] D.I. Townsend, J.C. Tou, *Thermochim. Acta* 37 (1980) 1.
- [10] M. Ahmed, H.G. Fisher, A.M. Janashek, *Proc. Int. Symp. Runaway Reactions, AIChE, CCPS, Ichem, Cambridge, MA, USA*, March 1989, p. 331.
- [11] *Emergency Relief System Design using DIERS Technology, DIERS Project Manual, AIChE, New York*, 1992.