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Identification of the Decomposition Products in an Industrial Nitration Process under Thermal Runaway Conditions

Angelo Lunghi,* Miquel A. Alós,† Lucia Gigante, Joan Feixas,† Eugenio Sironi, Josep A. Feliu,† and Paolo Cardillo
Stazione Sperimentale per i Combustibili, Viale A. De Gasperi, 3-20097 San Donato Milanese, Italy

Abstract:
Directive 96/82/EC on the control of major-accident hazards involving dangerous substances, so-called Seveso II Directive, requires inventorying of dangerous substances which are believed might be generated during loss of control of an industrial chemical process. In the present work a nitration process that has underlined a potential risk of thermal runaway has been studied. A kinetic model has been developed and validated using the calorimetric data from a Mettler RC1 and a differential scanning calorimeter, along with the commercial software BatchCAD. The model has been later used to simulate the behaviour of an industrial reactor under abnormal conditions and to evaluate their consequences. Finally, the conditions that lead to thermal runaway scenarios have been reproduced to identify the decomposition products, as Seveso II Directive requires, using thermogravimetry and adiabatic calorimetry coupled with FTIR gas analyser.

Introduction

Major accidents in chemical industry are one of the most hazardous types of industrial incidents due to the toxicity and amounts of substances handled at chemical factories and chemical warehouses. Not only do these substances damage the installations, but they are also a threat to human beings and the environment. Examples of these facts are the accidents at Flixborough (Great Britain, 1974), Seveso (Italy, 1976), Bhopal (India, 1984) and Basel (Switzerland, 1986) which seriously affected the population and the environment around these industrial installations.

To reduce the frequency and consequences of major accidents in the chemical industry, the European Community introduced several regulations and laws to enhance safety, prevention, and control at those installations where such events may occur. One of the last industrial safety normatives introduced by the European Community is the Council Directive 96/82/CE on the control of major-accident hazards, the so-called Seveso-II Directive. One of the topics of this directive is taking into account not only those substances produced or present at the industrial installations but also those that are "plausible" to be produced during "a loss of control of an industrial chemical process". Thus, companies are requested to assess the substances that may be produced due to this "loss of control of an industrial chemical process" so as to better design their safety policy.

* Author for correspondence. Telephone: +39 02 51604224. Fax: +39 02 514286. E-mail: lunghi@ssc.it.
† Hyprotech Europe, S.L., a subsidiary of Aspen Technologies Inc., Pg. Gràcia 56, 08007 Barcelona, Spain. Telephone: +34 932 156 884. Fax: +34 932 154 256. E-mail: joan.feixas@aspentech.com.

The request to take into account these "new" substances also introduces the need to define methodologies to assess them in the different accident scenarios. Literature review shows that most of the related methodologies are focused on determining the critical parameters to avoid the accident scenario, paying no attention to the products generated. On the other hand, the methodologies involved in the analysis of the evolved products require a high economical investment in instrumentation and experimentation only accessible to big companies. Furthermore, the instrumentation required by these methodologies is usually single-purpose, time-consuming, and not "easy-to-use", which is another serious handicap for those small and medium enterprises (SMEs) attempting to meet the directive requirements.

The objective of the present work is to design a short-cut methodology able to assess the toxic substances that may be produced due to "a loss of control of an industrial chemical process". A nitration reaction has been selected as a model for developing this methodology underpinned by (1)- the use of the calorimetric data obtained from the Mettler RC1 and other analytical techniques to define the kinetic model for the nitration and the decomposition reaction, (2) the simulation of the behaviour of the industrial process to obtain a set of parameters necessary to define operating safe conditions: the abnormal conditions of the system will be considered to obtain the runaway temperature plots, and (3) running proper tests in accord with the temperature profile obtained by the previous simulation, to identify the products generated during the thermal runaway as a response to the request introduced by the Directive 96/82/CE.

Methodology

Study of the Desired Reaction. We have studied a nitration reaction, carried out in homogeneous phase, under acidic catalysis, which a preliminary study indicated would be a potential runaway process. Nitration reactions are well-known as very reactive systems, and nitro derivatives often show tendencies for decomposition.[1] The kinetic behaviour of the reaction system has been studied by carrying out a series of isothermal reaction calorimetry (RC) experiments. The tests were run in semi-batch mode, adding nitric acid to the organic substrate, *N*-2-phenoxyphenyl-methanesulfonamide (FAM), over 1 h, using acetic acid as solvent and sulphuric acid as catalyst to yield the nitro compound derivative, *N*-(4-nitro-2-phenoxyphenyl)methanesulfonamide (NIM), and water, see Scheme 1.

The RC1 tests showed that the reaction is highly exothermic (adiabatic temperature rise of 50 °C); the shape

(1) Lunghi, A., Cardillo, P. *Riv. Combust.* **1997**, *51*, 1−2.

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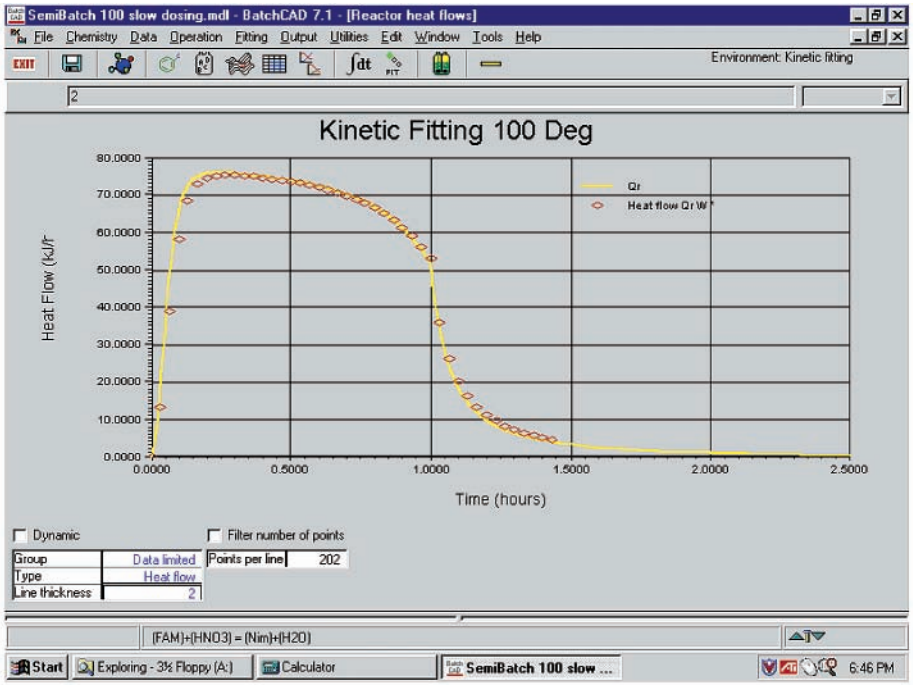

Figure 1. **BatchCAD-fitted plot for the RC isothermal experiment at 100 °C.**

Scheme 1. **Reaction scheme for the studied nitration step**

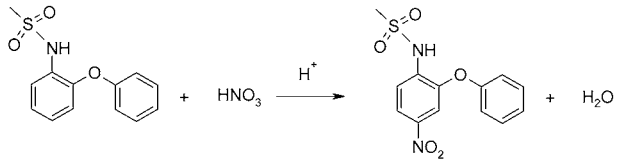

Table 1. **Heat of Reaction for the nitration process determined from RC1 tests at different temperatures**

experiment	temperature, °C	Q_r obtained (kJ/mol_{FAM})	heat of reaction reaction mixture (kJ/kg)	adiabatic temperature rise (°C)
1	80	178	102.57	49.8
2	90	177	102.87	51.1
3	100	175	105.71	49.8

Standard RC1 experiment condition: 43.4 g of HNO_3 (65% w/w) were added over 1 h into a solution of 110 g of FAM in 530 g of glacial acetic acid.

of the RC curves obtained is the typical one for a reaction that accumulates a percentage of reactant. When decreasing the temperature, accumulation increases; however, at higher temperatures, nitric acid starts to oxidise the organic substrate instead of nitrating it.[2] The reaction is usually done at around 90 °C. Table 1 summarises the calorimetric data at three different temperatures.

The kinetic equation proposed to describe the system is

$$\mathrm{FAM} + \mathrm{HNO_3} \rightarrow \mathrm{NIM} + \mathrm{H_2O} \quad R = k_1 \cdot \mathrm{FAM}^n \cdot \mathrm{HNO_3}^m \qquad (1)$$

The reaction orders with respect to the FAM, *n*, and to the nitric acid, *m*, that give the best fit of the heat flow versus time curves were determined using the "kinetic fitting environment" of the software BatchCAD[3] from each isothermal experiment. When the best orders were found and fixed ($n = 1$, $m = 2$), the experimental data were fitted again to find the best value for the rate constant at the three different temperatures. Figure 1 shows the regression plots for the RC isothermal experiment at 100 °C.

The activation energy and the frequency factor for the desired reaction were determined according to the Arrhenius equation from temperature dependence. The calculated values are the following:

$$E_a = 90.7 \text{ (kJ/mol)} \quad A = 4.76 \times 10^{11} \text{ (1/s)}$$

This kinetic data were assumed to model the thermal behaviour of the studied reaction.

Study of the Decomposition Reaction. The final reaction mass is much more thermally unstable than the pure product, NIM, itself. Therefore, the decomposition reaction involving the nitrated product and the reaction mass at the end of the process was studied. Preliminary DSC runs showed that the reaction mass starts to decompose at around 230 °C during a standard dynamic test (scanning rate 10 °C/min, static nitrogen atmosphere, sealed steel crucible medium-pressure-resistant) releasing 220 J/g. A method based on isothermal DSC run at different temperatures that was developed by Chervina and Bodman[4] for deriving kinetic equations of thermally unstable chemicals was used. The final reaction mass was analysed. Heat flow versus time experimental data from isothermal DSC at 190, 200, 210, 220, and 230 °C were collected and converted into conversion versus time data.

By analysing the curves in Figure 2, it can be seen that there was no apparent reaction going on at the beginning of

(2) *Enciclopedia della Chimica* (*Encyclopedia of Chemistry*, Engl. Transl.); Uses, Edizioni Scientifiche: Firenze, 1983.

(3) *BatchCad*, version 7.2 User's guide; http://www.hyprotech.com/batchcad/default.asp. Accessed 2002.

(4) Chervina, S., Bodman, G. T. *Process Safety Progr.* **1997**, *16*, 94.

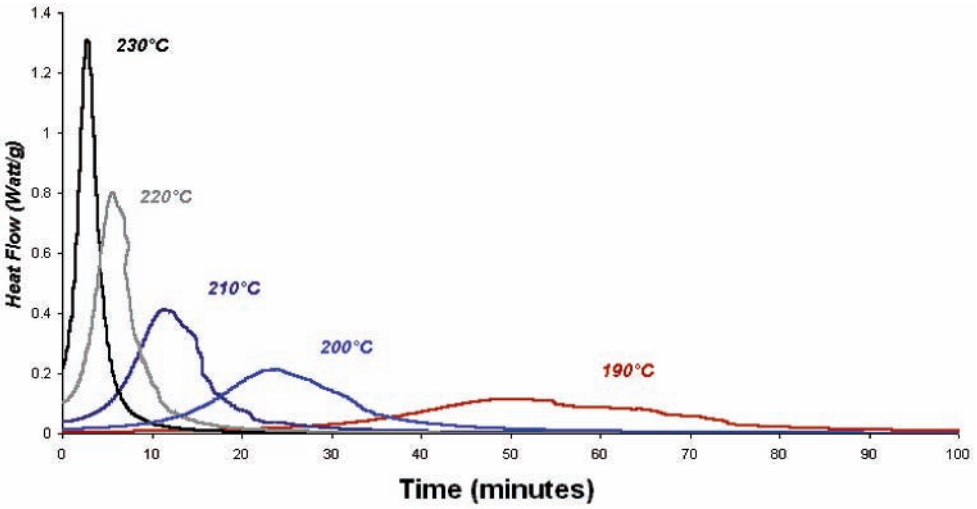

Figure 2. **Isothermal DSC curves at different temperatures.**

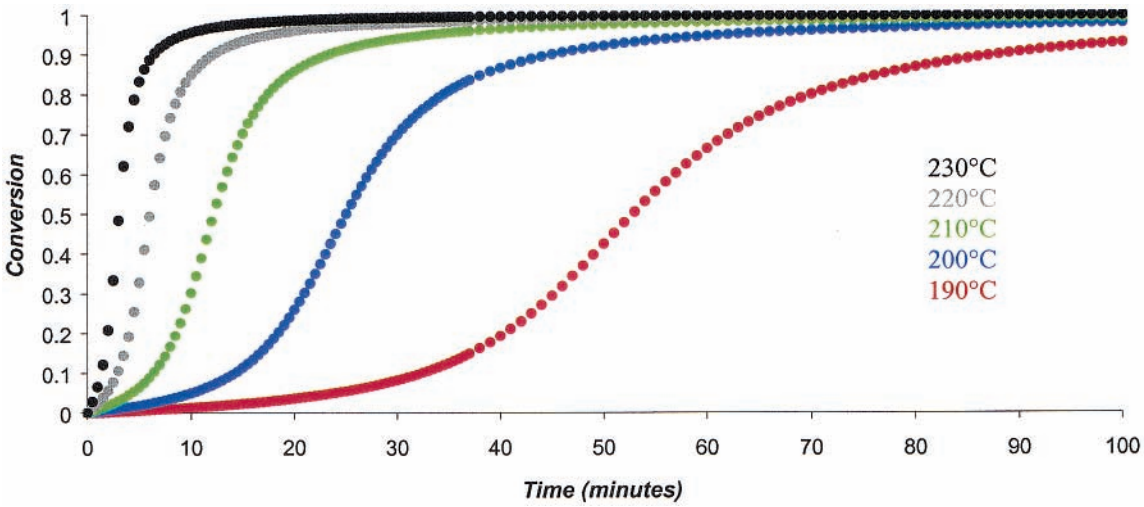

Figure 3. **Conversion vs time curves at different temperatures.**

Table 2. **Integral Heats and onset times for the decomposition Reaction determined from DSC runs**

DSC curves (°C)	integral heat (J/g)	onset time (min)
230	257.96	1.3
220	283.15	2.5
210	266.35	6.0
200	249.77	11.9
190	256.58	32.2

any isothermal run. After a variable induction time that increased when decreasing the temperature, the rate of the reaction began to accelerate and went through a maximum. The integral heats and the onset time are reported in Table 2.

Furthermore, the conversion versus time curves shown in Figure 3 are all S-shaped.

According to the experimental results, a series of kinetic models were proposed; the best-fitting were obtained with the following:

$$\mathrm{A} \rightarrow \mathrm{B} \quad R_1 = K_1.C_\mathrm{A}^n \tag{2}$$

$$\mathrm{A} + \mathrm{B} \rightarrow 2\mathrm{B} \quad R_2 = K_2.C_\mathrm{A}^n.C_\mathrm{B}^m \tag{3}$$

where:

A:	final reaction mass
B:	decomposition products
K_1 (s^{-1})	kinetic constant for initiation reaction
K_2 (s^{-1})	kinetic constant for autocatalytic reaction
n	reaction partial order for A
m	reaction partial order for B

Two competing reactions take place simultaneously: eq 2 is a slow initiation reaction, whereas eq 3 is the autocatalytic reaction. The former produces the catalyst B (a decomposition product not present initially in the reaction system) and allows the autocatalytic reaction to commence. This reaction scheme justifies the forms of the DSC curves and also the S-shaped conversion data which are characteristic of this autocatalytic behaviour.

The partial reaction orders with respect to the reactant A (final reaction mass), n, and to the catalyst B (decomposition products), m, were fitted from the conversion versus time profiles using BatchCAD. Results are shown in Table 3.

After the reaction orders n and m were determined from all isothermal experiments, they were rounded and fixed as $n = 2$ and $m = 1.5$, and the fitting procedure was repeated to determinate the isothermal rate constants. Results are summarised in Table 4. Finally, the activation energies and frequency factors were determined from the temperature

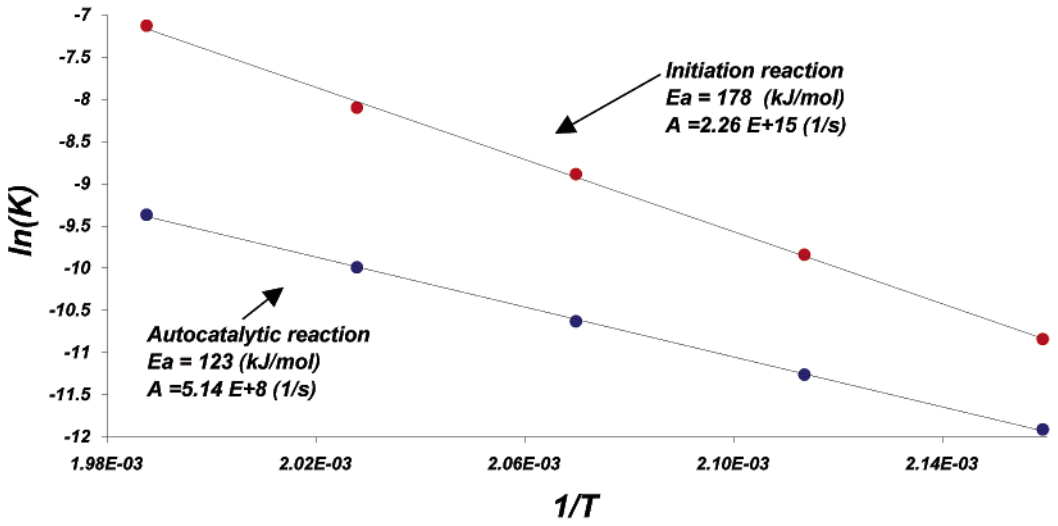

Figure 4. **Activation energy and frequency factors determination.**

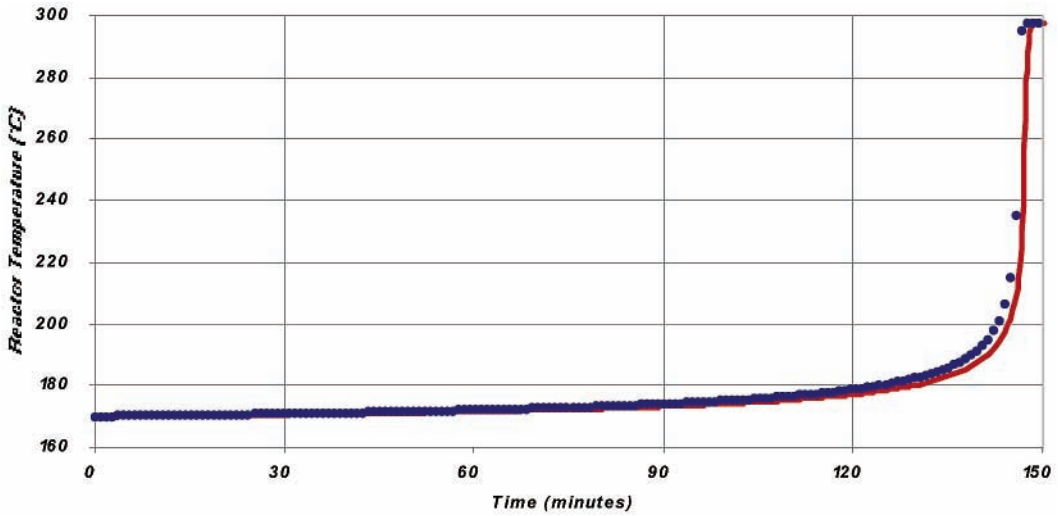

Figure 5. **Simulated (continuous line) and experimental (dotted line) behaviour of the final reaction mass decomposition under adiabatic conditions.**

Table 3. **Partial reaction orders with respect to the final reaction mass, n, and to the autocatalytic products, m, for the decomposition reaction**

DSC curves	*n*	*m*
230	1.98	1.50
220	1.94	1.45
210	1.93	1.44
200	1.98	1.52
190	1.86	1.47

Table 4. **Isothermal rate constants determined for the decomposition reaction from DSC runs**

DSC curves	K_1 (1/s)	K_2 (1/s)	K_1/K_2
230	8.09×10^{-4}	8.55×10^{-5}	9.43
220	3.05×10^{-4}	4.58×10^{-5}	6.65
210	1.39×10^{-4}	2.42×10^{-5}	5.72
200	5.34×10^{-5}	1.29×10^{-5}	4.14
190	1.96×10^{-5}	6.71×10^{-6}	2.92

dependence of the rate constants for the autocatalytic and the initiation reactions. The calculated values for both reactions are presented in Figure 4.

The combination of eqs 2 and 3 and the calculated values from Figure 4 gives the following rate equation for the decomposition reaction:

$$R\ (\mathrm{kmol/m^3\,s^{-1}}) = 2.25 \times 10^{15} \cdot \mathrm{e}^{-178000/RT} \cdot C_\mathrm{A}\left(1 + \frac{C_\mathrm{A} \cdot C_\mathrm{B}^{1.5}}{4.38 \times 10^{6} \cdot \mathrm{e}^{-54600/RT}}\right) \quad (4)$$

Equation 4 was verified by simulating, using BatchCAD, an adiabatic decomposition of the final reaction mass in an ARC test cell and comparing the simulation results with the experimental ones. The ARC curve is not ϕ-corrected since the simulation takes into account the thermal inertia factor of the adiabatic experiment. The ARC experiment conditions are summarised in Table 5. Due to the high reactivity of the reaction mixture, the ARC test has been performed filling the test cell with a small amount of sample. Figure 5 shows the observed and calculated adiabatic temperature plots. The good overlay between both curves confirms the validity of the developed eq 4.

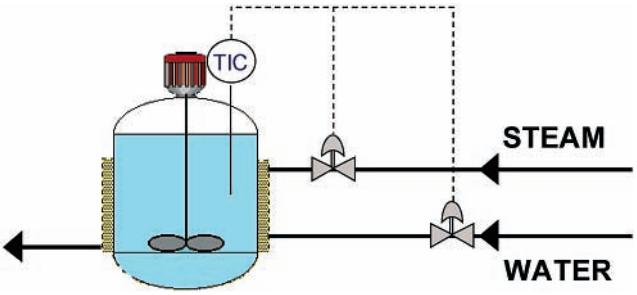

Figure 6. **Fluid conditions are steam at 130 °C, 2.7 bar (max flow 4520 m^3 h^{-1}) and cooling water at 20 °C (15.5 m^3 h^{-1}).**

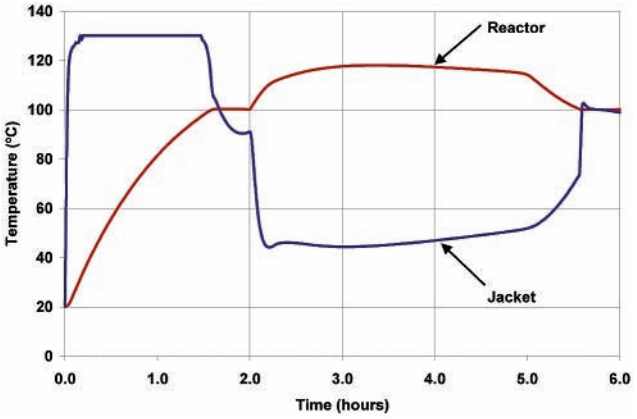

Figure 7. **Jacket and reactor temperature profile under normal conditions (initial reactor temperature 100 °C).**

Table 5. **ARC experimental conditions**

Bomb	Hastelloy C
Φ factor	2.20
method	Iso-Aging
start temperature	170 °C
sample weight	3.75 g

Industrial Process Simulation. Industrial process simulation is done using a 9.09 m^3 reactor from the Pfaudler RA series database available in BatchCAD. The heat-transfer system comprises two service fluids that are fed into a 1.45 m^3 jacket on a drain/fill mode. A proportional controller allows heating and cooling of the reactor to the appropriate operation temperature. Figure 6 illustrates the described configuration.

During normal operating conditions, the reactor is charged with 4.7 m^3 of a mixture composed of 20 mol % FAM and 80 mol % acetic acid. A second mixture made of 34 mol % HNO_3, 2 mol % H_2SO_4, and 64 mol % H_2O is then charged in semi-batch mode, (0.463 m^3 h^{-1}), during 3 h. Under these conditions, no accumulation of nitric acid occurs in the reactor, and the temperature profile could be classified as QFS (quick onset, fair conversion and smooth profile).[5] Figure 7 shows reactor and jacket temperatures as function of time.

The process has been then simulated under abnormal conditions. Scenarios that can lead to a runaway have been reported in several works in the literature.[6−8] Two typical examples are coolant failure and inadequate agitation. Both scenarios have been simulated using BatchCAD. In the first example, Figure 8, the process is running under normal conditions; however, after 1 h of mixed acid dosing, the cooling service is disabled by blocking the valve. The process becomes virtually adiabatic, and the decomposition temperature is reached.

In the second case, Figure 9, the stirrer is accidentally stopped after 1 h of dosing. As a consequence, the reactor heat-transfer coefficient falls to low values, and the process runs close to adiabatic conditions. Note that decomposition temperature is reached earlier than in the previous scenario.

Analysis of the Decomposition Products. To study the products generated during the runaway scenario as response to the requirements introduced by the European Directive 96/82/EC, we carried out experiments with a thermal balance (TG). The decomposition products released were conducted with a nitrogen flux through a heated transfer line to a FTIR equipped with a gas cell. A picture of this equipment is shown in Figure 10.

To obtain information on "reasonable decomposition products" that may be produced due to "a loss of control of an industrial chemical process", the temperature profile obtained using BatchCAD for the two abnormal scenarios was reproduced in a TGA analyser. The TGA test was run under nitrogen atmosphere with a flow rate of 75 mL/min, using an open platinum crucible, connected to a FTIR gas analyser to identify the decomposition gases and vapours.

The results of these tests showed that the reaction mixture releases acetic acid (the solvent of the reaction) at the beginning of the test. When the temperature increases, the residual mass decomposes releasing:

SO_2	reference IR peak 1377 cm^{-1}
methane	reference IR peak 3020 cm^{-1}
methanol	reference IR peak 1040 cm^{-1}
benzene	reference IR peak 671 cm^{-1}
nitro-derived compounds such as nitroaniline	

The decomposition products have been recognized zooming the spectrum of the gaseous mixture in the zone of typical peak (e.g., the typical IR peak of SO_2 at 1377 cm^{-1}) and comparing it with the proper FTIR spectrum DB. Figure 11 shows the sprectrum of the gaseous mixture and the spectra for the identified pure compounds. NO_2 is probably also produced, but the FTIR analyser is not able to detect it. This methodology has been developed only to verify if some dangerous decomposition products, detectable by FTIR, are formed. However, the methodology could be improved by coupling a GC−MS technique to the current instruments. This will increase the window of detection for detectable products and allow quantifying them, as it is required in the

(5) Steensma, M., Westerterp, K. R. *Ind. Eng. Chem. Res.* **1990**, *29*, 1259.

(6) Barton, J., Rogers, R., Eds. *Chemical Reaction Hazards: A Guide to Safety*; Gulf Publishing Company: Houston, TX, 1997.

(7) Health & Safety Executive, Design and Operating Safe Chemical Reaction Processes, 2000.

(8) Cardillo, P. *Incidenti in ambiente chimico. Guida allo studio e alla valutazione delle reazioni fuggitive* (*Accidents in Chemical Environment: A Guide for Studying and Evaluating Runaway Reactions*, Engl. Transl.); Stazione Sperimentale per i Combustibili, San Donato Milanese, 1998.

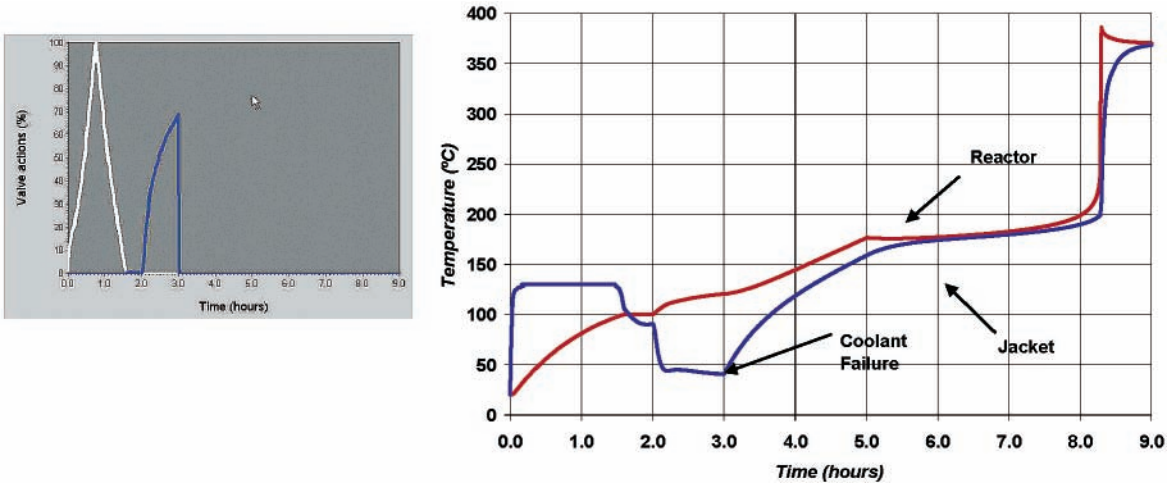

Figure 8. **(Left) Percent opened valves for the heating (white line) and cooling (black line) service fluid. (Right) Jacket and reactor temperature profile after a coolant failure at time equal to 3 h.**

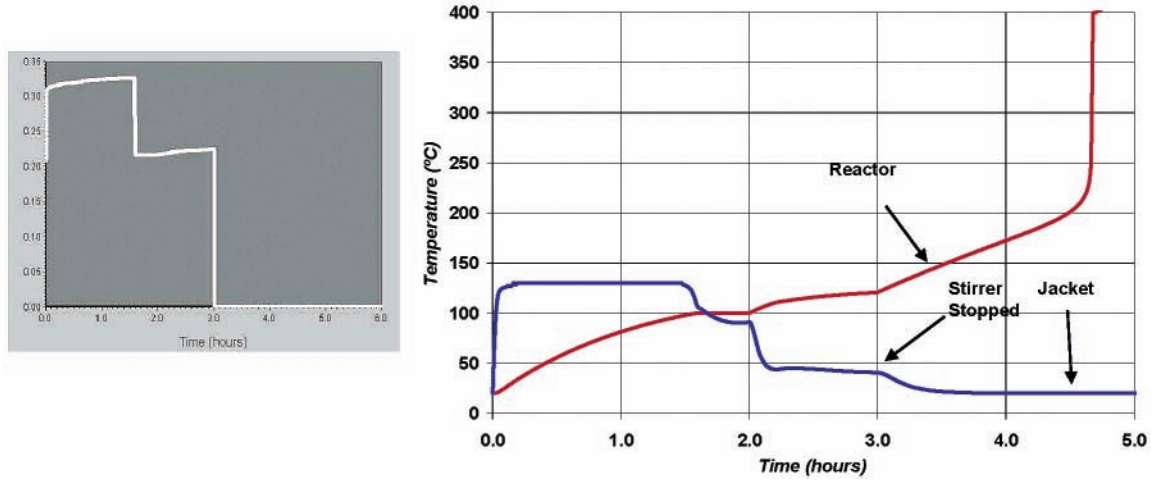

Figure 9. **(Left) Overall reactor heat transfer coefficient. (Right) Jacket and reactor temperature profile when stirrer fails at time equal to 3 h.**

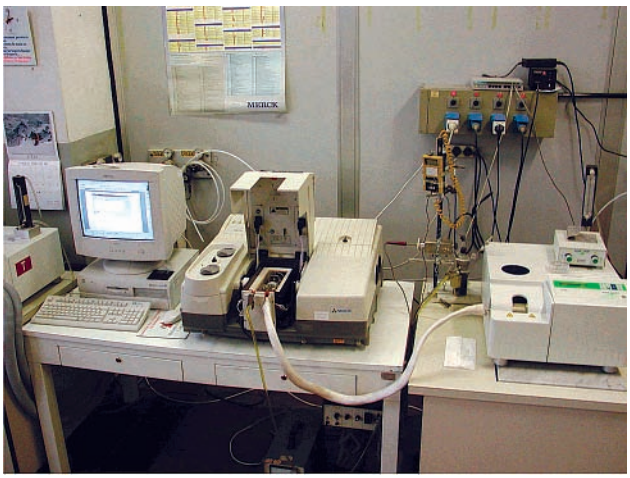

Figure 10. **Picture of the equipment (TG + FTIR) used to identify the decomposition products.**

Seveso II directive. The residual mass after the heating proved to be virtually insoluble in any of the solvent mixtures we tried out. Therefore, GC−MS or HPLC−MS techniques achieved no identification of high-molecular weight residual components when analysing these extracts.

Conclusions

The present work shows a short-cut methodology able to identify the toxic substances that may be produced due to "a loss of control of an industrial chemical process", as is required by the Seveso II Directive.

Limited targeted experiments in the Mettler RC1 and the DSC along with the kinetic capabilities of the software BatchCAD easily allow obtaining an accurate kinetic model of the chemical system. The mentioned software allows the modelling of an industrial reactor and the simulation of the whole process, permitting the identification of safe operating conditions. The model has been used also to simulate the behaviour of the industrial reactor under abnormal conditions. The resulting temperature profiles have been verified experimentally in an adiabatic calorimeter. These profiles have been reproduced in a thermal balance to generate and then identify the decomposition products by using TGA coupled with a FTIR gas analyser. The proposed methodology will be improved by coupling a GC−MS analyzer to the current instrumentation so that the window of detection for detectable products will be increased.

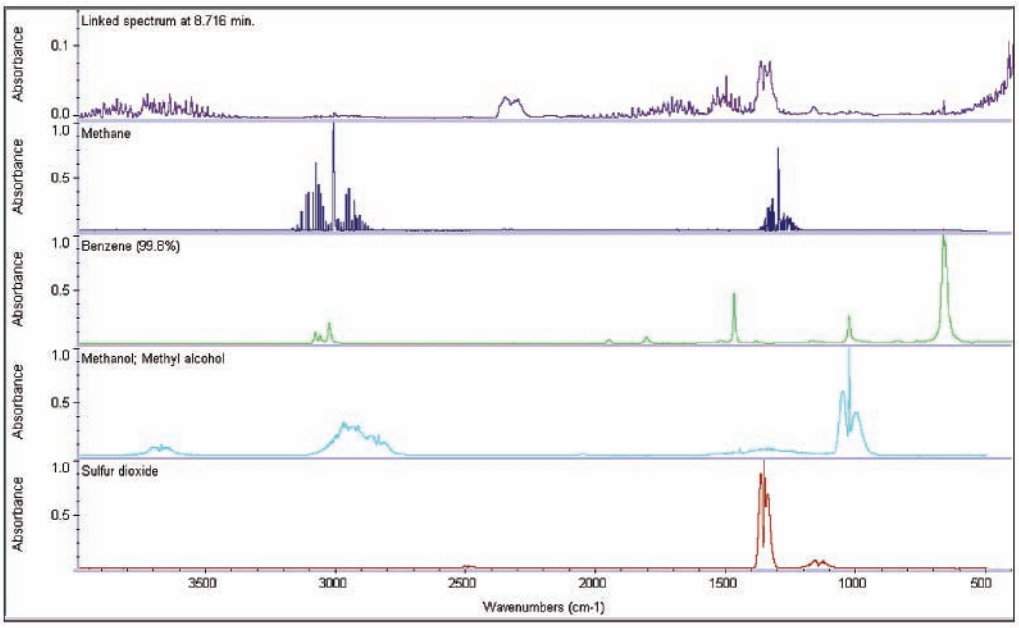

Figure 11. **Search results in the FTIR spectra DB.**

Acknowledgment

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(9) Web Site: http://www.harsnet.de/. Accessed 2002.