Process Improvements From Incident Data

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Abstract: This paper will discuss four different chemical processing accidents that resulted from plant mal-operations. Each incident was relatively minor yet provided valuable information about the stability and/or vulnerability of the process to upset conditions. The reaction classes involved were:

- Polyester polymerization
- Secondary amine formation followed by decomposition
- Oxidation of poly-alkylated aromatic hydrocarbon
- Base catalyzed Oligomerization

The paper describes the 'after-the-fact' data that was obtained by calorimetric hazards testing. We will discuss how the information was used, in each case to improve the process safety of the particular operation.

We will also describe an incident database that may be used by chemical companies to provide an on-going ranked and categorized record of accidents and incidents that have occurred. The value of the database information lies in the fact that the actual and potential severity of each accident is estimated from the data of the incident events. This information can be used to distinguish processes that may be responsible for the majority of the minor accidents from those processes where more severe, but infrequent, incidents occur. The information is also valuable in providing a focus with which to drive process safety improvement efforts.

1. INTRODUCTION

It is regrettable but true that the chemical processing industry (CPI) has continued to experience accidents and incidents involving the chemistries associated with the manufacturing process. Accidents and incidents also continue to occur that are solely traceable to equipment and mechanical failures but those events are not the subject of this presentation. The term "chemistry" is used, in this context, to include

- handling and storage of the reagents and products;
- interactions of the reagents and products with materials of construction;
- desired chemical reactions that occur in the reactor
- undesired chemical reactions that may occur in the reactor vessel, and/or
- chemical reactions due to inadvertent mixing.

Barton and Nolan [1] analyzed 189 incidents that occurred in the UK during 1962 through 1987. The information was obtained from the Health and Safety Executive (UK equivalent to OSHA). Of the 189 incidents 34% were polymerization, 15% resulted from nitration or sulfonation, and 5% were from hydrolysis reactions. Other reactions involved were salt formation, halogenation, alkylation, amination, diazotization, oxidation and esterification. The identity of the top two or three manufacturing chemistries involved is probably no surprise. Polymerization chemistry is by far the most prevalent chemistry practiced today and accumulation of reactants is a common characteristic of this process when carried out in a batch or semi-batch manner.

When these 189 incidents were analyzed by cause, lack of knowledge of chemistry and thermochemistry accounted for 20% of the incidents. In other words, every fifth incident could

have been mitigated, and maybe prevented, if process knowledge had been available regarding the thermodynamics of the reaction and its impact on the design engineering function. The other 80% could be described as errors in plant design and/or operation. Of these temperature control (32%), mis-charging (35%) and maintenance (25%) were the top three primary causes. The bottom line is that what you don't know can/will hurt you.

Four recent, relatively minor, accidents have been selected to illustrate the results of incomplete process safety information. The role of hazards testing, and the information gained from each accident, will be described.

The incidents will be presented in the following manner:

- Incident description
- What process information was known and not known
- What was learnt during the investigation, including how the data were obtained
- What process improvements were implemented

It will be seen that temperature control and heat removal played a significant role in the four events.

We will also briefly describe a incident database that produces a severity ranking list for chemical process accidents. An empirical algorithm is used to derive the severity ranking from the accident data obtained during the investigation.

Recently, McIntosh and Rogers Taylor [2] have described an incident database that classifies an incident by the location, equipment involved, type of chemistry performed, etc. However, no

severity estimate is provided for the recorded incident. This database is similar in structure and intent to the analysis of UK incidents provided by Barton and Nolan [1]. Fernando ([3] reminds us that "reporting near misses can help avoid incidents." He succinctly develops the case for not only reporting the facts of accidents but also assigning a severity rating to the accident. Fernando substantiates his thesis through the accident frequency/severity ratios work of Heinrich and Bird.

2. INCIDENTS

2.1 Polyester polymerization

The chemistry involved was a batch addition of an anhydride to a conventional polyester monomer blend comprising an unsaturated hydrocarbon and a glycol mixture. The procedure had been performed several times before at 75% of full scale without incident and had been run at full manufacturing scale three times prior to the accident.

2.1.1 Incident Description

Following the addition of the hydrocarbon and glycols to the reactor the reaction mass was heated quickly to 120°C. The total charge of the anhydride added over 15 minutes. However, the process required that the addition temperature was 105°C and the addition rate limited to 45 minutes. The process was run in mid-summer when the weather conditions were 97°F and about 70% relative humidity. These facts were subsequently established, during the incident investigation, from NOAA (National Oceanographic and Atmospheric Agency) by accessing the meteorological data from the nearby international airport via the Internet (www.ncdc.noaa.gov).

The reactor temperature rose as expected by about 40°C, held reasonably constant under full cooling, but began to rise again some twenty minutes later. Within a further forty minutes, the temperature had risen to over 200°C at which point the operators withdrew from the structure. The reactor's rupture disk blew and the contents of the reactor were ejected through the vent stack (15 feet total length with a 90 bend in the middle) some 200 yards. There were no injuries and the reactor was undamaged.

2.1.2 Available Process Information

The process information available to help explain the cause(s) of the incident suggested that the runaway was possibly caused by failure of the cooling system. Cooling was derived from a plant wide cooling tower water loop from which five reactors obtained cold water on demand. The cooling tower was due for renovation/replacement within one year from the date of the incident. Thermal stability of the reactants and the consequences of loss of cooling, at critical stages in the process, were not known. The power output of the desired reaction had been estimated qualitatively from a single laboratory resin kettle run.

2.1.3 Incident Investigation Results

The incident investigation was conducted using a root cause approach within 24 hours of the incident. Several questions arose relating to the thermal stability of the reactants and product for which there was no immediate data available.

Low thermal inertia adiabatic calorimetry (Figure 1) was used to simulate the conditions of the runaway. The nature and extent of the runaway under the conditions of loss of cooling were rapidly determined. The cause of the runaway, together with the extent of the runaway, was

deduced from the data (Figure 2). Batch reaction manufacture with all the anhydride added rapidly had apparently led to a minimal margin of safety for the difference between power generation from the reaction and the cooling system's heat removal capability. The use of NOAA air temperature data (www.ncdc.noaa.gov) provided the actual high and low temperatures for the day of the incident. This information was used to demonstrate that at the time of the incident the cooling tower efficiency was insufficient to provide the cooling needed during the high rate of anhydride addition.

2.1.4 Process Improvements

A series of process changes were made that restricted the addition rate of the anhydride. This was achieved by using an intermediate shot tank, one third the volume of the full anhydride charge and limiting its addition rate to the reactor. The basis for this approach had been developed the data obtained from heat flow reaction calorimetry (Figure 3). Adiabatic calorimetry was also used to verify that the emergency relief devise was sized correctly for a runaway reaction in case all of the one-third charge of anhydride was batch added to the reactor.

2.2 *Secondary Amine Formation*

Pilot plant studies had shown that this reaction could be run either in a batch or semi-batch mode. The required cooling duties were significantly different for the two modes. These studies had indicated that the batch additions of the chlorinated hydrocarbon to the amine, at elevated temperatures, could be difficult to control thermally and so full-scale manufacture was started at ambient temperature with all reactants present in the reactor. The process in question was run at least twenty times prior to the incident. Temperature excursions of 10 – 20°C had been experienced in some of the runs

2.2.1 Incident Description

The batch proceeded normally with heat being applied to the reactor after a full charge of reactants had been added. The reaction exotherm led to the expected increase in temperature, however, when operators switched over to cooling the reactor temperature continued to climb. The subsequent runaway reaction was contained within the plant's vent header and catch tank. There was no loss of containment to the outside.

2.2.2 Available Process Information

Data from the pilot plant studies provided an indication of the power output of the reaction when performed at elevated temperatures. However, no pilot plant information was available that was applicable to the process being performed at the manufacturing scale or about the procedures being used at the time of the accident.

2.2.3 Incident Investigation Results

The exact reaction recipe and the finished product were tested using high thermal inertia adiabatic calorimetry. The results showed that the reaction was exothermic leading to an adiabatic temperature rise of about 190°C. This temperature rise would be sufficient, in the event of a major loss of cooling capability, to lead to product decomposition. The decomposition reaction was strongly exothermic and produced significant quantities of gaseous decomposition products.

Figure 4 illustrates the result of mixing the reactants at ambient temperatures in an adiabatic environment. The mixture exhibits a self-sustaining exotherm beginning at 45°C. The temperature/time plot (Figure 4) shows that the desired reaction is nearing completion, under adiabatic conditions, at around 170-180°C. However, the decomposition runaway reaction is well underway at this point, as shown by the saddle point in the temperature/time curve. These deductions were confirmed by performing the same test on the reaction product that showed an

identical trace through the 210-350°C temperature range but without the thermal activity from 45-200°C

2.2.4 Process Improvements

Reaction calorimetry was used to demonstrate that the controlled addition of the chlorinated hydrocarbon to the amine, over a period of about one hour at 135°C, produced the correct product. This process change did not give rise to the potentially dangerous accumulation of unreacted reactants that had led to the runaway reaction.

2.3 *Oxidation of poly-alkylated aromatic hydrocarbon*

The oxidation of a ring-alkylated aromatic hydrocarbon, using nitric acid, at elevated temperature and pressure, was accomplished by the controlled addition of cold nitric acid to the reactor running at 165°C and 25 psi. Internal cooling coils mounted about six feet above the bottom heater of the reactor. The process had been run for at least a year. Several significant temperature excursions had been experienced that were all controlled by the cooling system.

2.3.1 Incident Description

The addition of the solid poly-alkylated aromatic was completed and the temperature raised to melt it. Addition of nitric acid was started at 135°C with the temperature and pressure expected to rise and level off at 165°C and 25 psi respectively. Shortly after the feed was commenced the temperature rose to over 300°C in less than one minute blowing the rupture disk. The material ejected from the vent was contained within the vent system although the vent header suffered some minor damage.

2.3.2 Available Process Information

The oxidation of the alkylated hydrocarbon was known to be exothermic with the possibility of nitration occurring at temperatures lower than those used in the process. The addition of nitric acid, giving rise to undesired nitration, leads to exothermic reactions that produce large quantities of non-condensable gases.

2.3.3 Incident Investigation Results

High thermal inertia adiabatic calorimetry for the addition of nitric acid to hot and cold hydrocarbon provided the basic data needed to begin to understand the cause of the incident. The data also clearly distinguished between the oxidation and nitration reactions.

2.3.4 Process Improvements

Selection of the most credible worst case scenario for the oxidation process was followed by low thermal inertia adiabatic calorimetry designed to generate the data needed to design an adequate emergency relief system for the reactor, figure 5. The calorimetric data also provided most of the information that was used to define the Basis of Safety for the process and helped to establish the Limits of Safe Operation.

2.4 *Base catalyzed Oligomerization*

A base catalyzed oligomerization was performed without significant incident for several months. The plant would periodically experience minor reaction energy spikes anywhere from 15 to 60 minutes into the base addition part of the run. During a process hazard review, following a particularly energetic power spike at the plant, it was recommended that the process be studied in detail to discover the cause of the unpredictable energy spikes.

2.4.1 Incident Description

The unexpected chemistry occurred in the consultant's laboratory rather than in the plant. High and rapid energy output was noted when the reaction was performed in both the adiabatic calorimeter and during isothermal calorimetry after about 15% of the base was added to the reactor for each run performed. These laboratory results did not agree with the plant observations. Based on the lab data a serious runaway reaction should have occurred several times in the past. However, plant history indicated that only temperature deviations of some 30°C had been seen, up to the time of the incident. period.

2.4.2 Available Process Information

The process information needed to reduce the risk of running the process was already known to the client company although the current group of process engineers were not aware of the reasoning behind certain aspects of the process details. In particular, the fundamental reason for keeping a heel in the reactor from batch to batch was not fully appreciated by this group. It also transpired that the company had recently undergone a downsizing and the key lead operator had retired.

2.4.3 Incident Investigation Results

The undesired reactions and the discovery of their cause, that occurred in the consultant's laboratory led to the development of the Basis of Safety for the company's process. Reaction calorimetry, performed in the absence and presence of a heel from the previous run, Figure 6, clearly demonstrated the function of the heel as a catalyst. Adiabatic calorimetry was performed to provide the required information for vent sizing the reactor for the worst-case scenario of missing heel at reaction startup.

2.4.4 Process Improvements

This information obtained from the calorimetry testing provided the Basis of Safety for the process, defined the needed administrative controls to ensure that the heel was always present for batch startup, and yielding the data necessary to verify the design of the emergency relief system.

3. ACCIDENT SEVERITY DATABASE

Using process accident data to improve the process safety performance of a company is one of the OSHA 29CFR1910.119 requirements. It is traditionally accomplished in two ways. The incident, immediately after it has occurred, is fully investigated and the results of the investigation, including process changes, are fully communicated. The data is also used to help remove a potential difficulty with the operation of the process.

However, there is a third important area of use for a company's incident information. The data can be used to rank the severity of the event. Moreover, the incident may also be judged in terms of it's potential for additional impact to the facility. In other words, an incident may be ranked by a number/letter code that indicates the severity of what actually happened (the number) together what potentially could have occurred (the letter).

Incident data can be classified into five main areas:

- *Incident data* – ΔH, T & P observed, duration of temperature and pressure excursions
- *Financial data* – damage, cleanup costs, business interruptions
- *Nature of the incident* – location, vessel type, incident type
- *Cause and Effect contributors* – root cause and side effects
- *Potential seriousness of the incident* – health, property, business and containment losses.
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Table 1 shows eleven incident related categories and details the specific items of two categories that are used to classify an incident. Each item within each category has a score associated with it; the higher the score the higher the seriousness of the event, within each category. For example, the severity for "Operating Procedures: Not Followed" is scored much higher than "Operating Procedures: Inadequate" which is, in turn, scored higher than "Operating Procedures: Will be revised"

Table 1. Incident Categories and Items for Two Categories

OPERATING PROCEDURES		INCIDENT CATEGORIES		VESSEL TYPE
Changed		• Incident location		Distillation Column
Inadequate		• **Vessel type**	➔	Drum, 55 gal
No Procedure		• Vessel damage		Exchanger
Not Applicable to Job		• Incident type		In-line Reactor
Not Followed	➔	• **Operating procedures**		Laboratory Rig
Procedures will be Revised		• Control schemes		Line, Valve
Shift Change		• Relief system		Process Drum or Tank
Shut Down, by design		• Material characterization		Pump, Compressor
Shut Down, crash		• Other associated causes		Rail Car/Tank Truck
Start Up		• Involvement		Reactor
Wrong One(s)		• Health damage		Storage / Feed Tank
		• Potential seriousness		Storage, Other
				Sample / Reagent Bottle
				Waste Container

This approach of applying a score to a large number of individual aspects of the incident leads to a reasonably unbiased numerical assessment of the severity of the incident. As noted above there are four other major categories where this scoring approach is used. The final rating score is scaled to give a rating of 1 through 5 for the actual severity and A through D for potential severity.

For example, an incident with a rating of 3B is a moderate incident but more could have happened if the in-place mitigation procedures had not been effective. An incident rated as 3A

indicates that all that could have happened actually occurred and the full effects of the incident (in this case a 3-rated event) were experienced by the facility

The incident database, briefly described here, is under development to provide a rating system for chemical process accidents. The approach will be such that the data of the incident drives the rating of the incident in a manner unbiased by different incident investigators. Success in the design of this rating system allows for a consistent rating of an incident from site to site and from company to company.

4. CONCLUSIONS

We have shown in this presentation, by way of four examples of chemical process accidents, that the appropriate and timely use of a few well designed calorimetric tests, using the correct equipment to simulate the main aspects of a chemical processing accident, leads to a solid understanding of the chemical and engineering causes of the incident. These same hazard-testing techniques can also provide a sound basis for subsequent process and safety improvements.

We have also briefly described a database for chemical process accidents that will provide estimates of the severity of the accident. The severity is derived from the data of the event and produces a numerical ranking of the severity of the upset together with an estimate of the potential seriousness of the accident.

5. REFRENCES

1. J. A. Barton and P.F. Nolan “Hazards X. Process Safety in Fine and Specialty Chemicals”, Paper 2, Inst. Chem. Eng., Symp. No. 115, 1989. Published by The Institute of Chemical Engineers, Rugby, UK.

2. J. A. McIntosh III and S. Rogers Taylor, Chem. Proc., 62, 31-38 (April, 1999).

3. D. Fernando, The Chemical Engineer, 28 September p.13 (1995).

Figures Referenced in Text

1. Adiabatic Test Cell up to 120ml.
2. 3 Radiant Guard Heaters
3. Calorimeter Assembly
4. Pressure Vessel – 3 liters
5. Direct Agitation
6. Magnetic Agitation
7. Insulation
8. Sample Thermocouple
9. Sample Pressure transducer
10. Vessel Pressure transducer
11. Connections for Injection, Venting, Disposal Systems

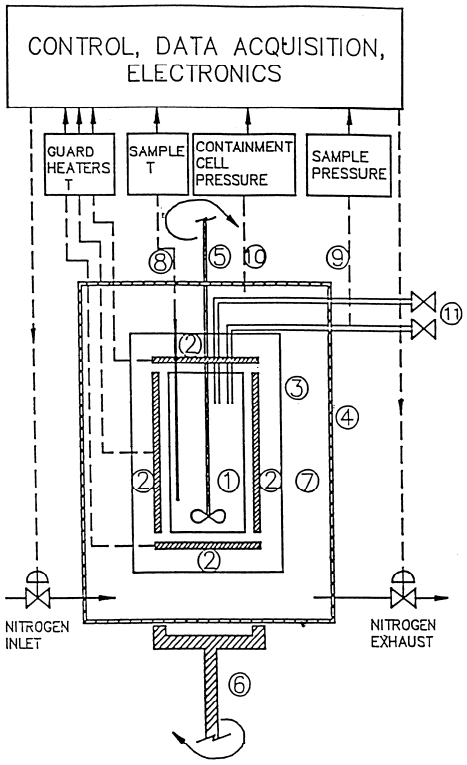

Figure1. PHI-TEC Adiabatic Calorimeter

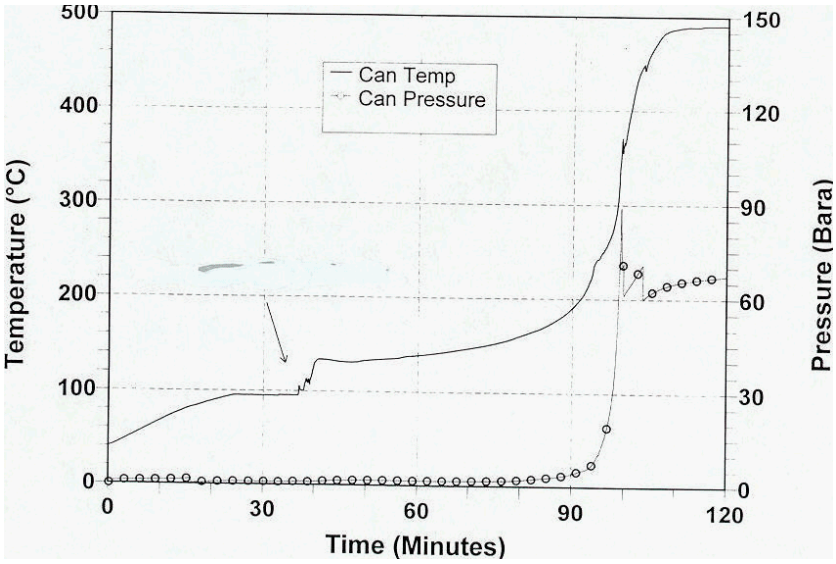

Figure 2. Adiabatic Calorimetry (PHI TEC) of Full Batch Anhydride Addition to Glycol/Unsaturated hydrocarbon

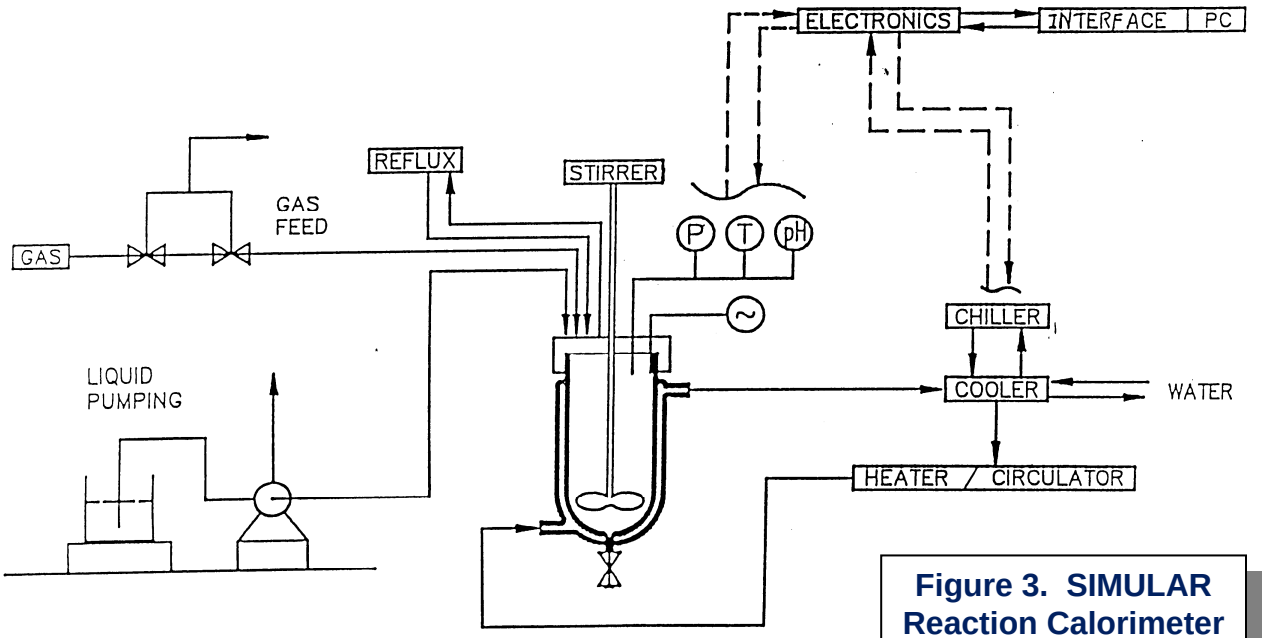

Figure 3. SIMULAR Reaction Calorimeter

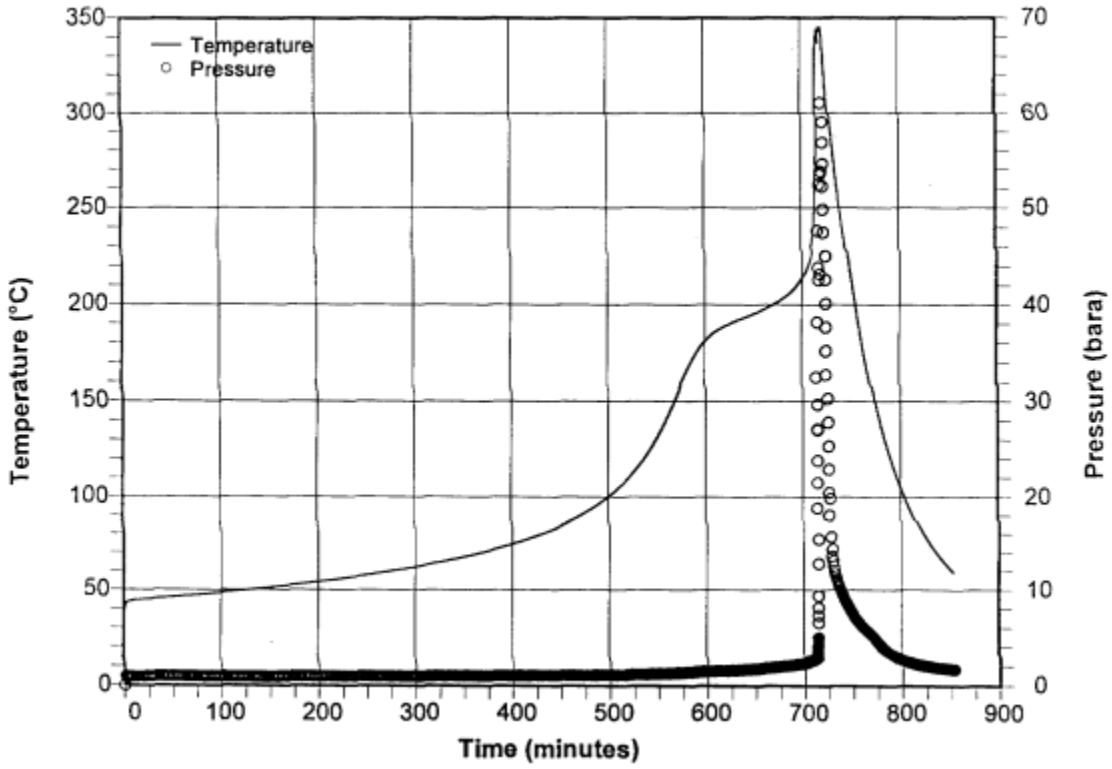

Figure 4. Adiabatic Calorimetry (PHI TEC) for Secondary Amine Reaction and Product Thermal Activity and Stability

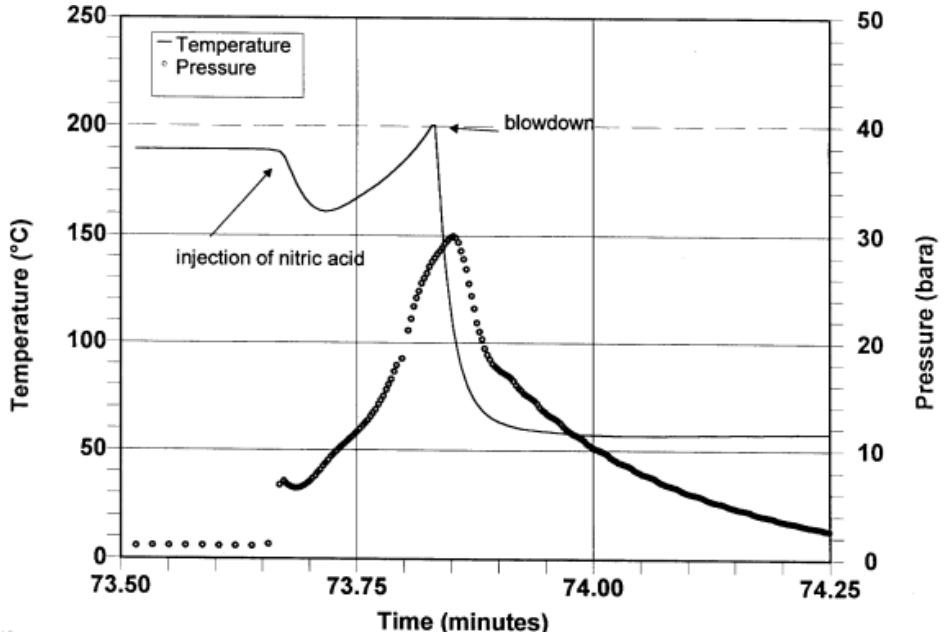

Figure 5. Adiabatic Calorimetry (PHI TEC) for Addition of Hot Nitric Acid to Reaction Mass

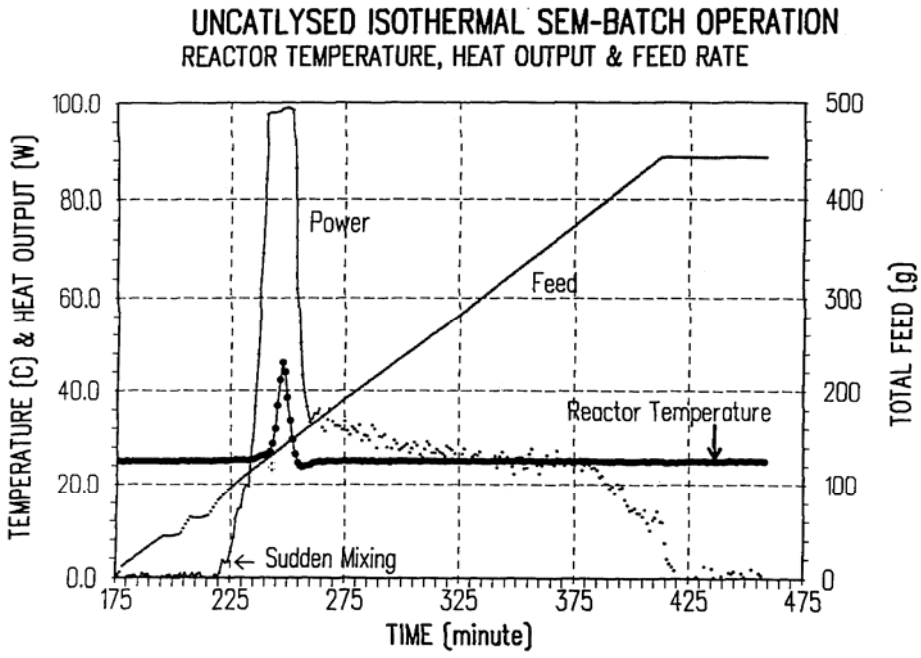

Figure 6. Isothermal Calorimetry (SIMULAR) for Catalyzed and Uncatalyzed Oligomerization Reaction